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HEAT SEAL FILM
[Hito Shiru Firumu]

Akio Toyota, Masao Uekura, Shoji Imamura,
and Takashi Mihara

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INVENTOR(S)	(72):	Akio Toyota, Masao Uekura, Shoji Imamura, and Takashi Mihara
APPLICANT(S)	(71):	Dai-Nihon Ink Chemical Industries Co., Ltd.
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Claim 1

A heat seal film which is a heat seal film constituted by a substrate layer & a heat seal layer and which is characterized by the facts that the aforementioned substrate layer is comprised of (A): A crystallized lactic acid-type polyester composition bearing a melting point of 120°C or above and inclusive of polylactic acid & a lactic acid-type polyester and that the aforementioned heat seal layer is comprised of (B): Either a non-crystalline polylactic acid bearing a softening point of 40 ~ 110°C or a non-crystalline lactic acid-type polyester composition bearing a softening point of 40 ~ 110°C and inclusive of polylactic acid & a lactic acid-type polyester.

Claim 2

A heat seal film mentioned in Claim 1 wherein the lactic acid-type polyester within the lactic acid-type polyester composition (A) includes lactic acid units & polyester units within a weight ratio range of 10 : 90 ~ 90 : 10 and bears a weight-based average molecular weight of at least 10,000 & a glass transition point of 60°C or below and wherein the ratio, within the aforementioned lactic acid units, of the L form to the D form (L/D ratio) or of the D form to the L form (D/L ratio) is confined to a range of 100/0 ~ 97

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in terms of the mass ratio thereof.

Claim 3

A heat seal film mentioned in Claim 1 wherein the storage modulus, at 20°C, of the lactic acid-type polyester within the lactic acid-type polyester composition (A) as it is stipulated by the Japanese Industrial Standards K 7198 method A is 2.5 GPa or below.

Claim 4

A heat seal film mentioned in Claim 1 wherein the minimal value of the storage modulus of said heat seal film at or below a temperature 20°C lower than the melting point thereof as it is stipulated by the Japanese Industrial Standards K 7198 method A is 40 ~ 4,000 MPa.

Detailed explanation of the invention

[0001]

(Technical fields to which the invention belongs)

The present invention concerns a heat seal film suitable for wrapping or storing various foods, beverages, chemicals, non-durable consumer goods, etc. subjected to thermal melt adhesions as well as a packaging container (e.g., packaging bag or case, light-weight container, etc.) obtained by thermally molding said film.

[0002]

(Prior art)

Immense quantities of plastics have been used in recent years, whereas discarded plastics have caused global environmental problems such as the shortage of landfill sites, hindrances of scenic sites, threats to oceanic organisms, environmental pollutions, etc. Plastics used generally as so-called "general-purpose resins" in the prior art are instantiated by polyethylene, polypropylene, polystyrene, polyvinyl chloride, polyethylene terephthalate, etc., whereas incineration & landfill methods have been practiced for disposing of these resins. These disposal methods are problematic, for, in cases where such resins as polyethylene, polypropylene, polystyrene, etc. are incinerated, furnaces tend to become damaged due to high combustion calories of these resins, and accordingly, furnace lives become shortened. Polyvinyl chloride, on the other hand, entails a low combustion calorie, although it is known to generate harmful gases at the time of incineration. In cases where these general-purpose resins are subjected to landfill disposals, furthermore, they are known to retain their original shapes on a semi-permanent basis without being degraded due to high chemical stabilities, thus serving as one factor contributing to the increasingly grave shortage of landfill space.

[0003]

In cases where they are carelessly discarded in natural environments, furthermore, scenic beauties may become adversely affected because of their stabilities, or they may become inadvertently ingested by oceanic organisms, birds, etc., resulting in the depletion of valuable living resources, and thus, they serve as a factor contributing to environmental destructions. Biodegradable polymers have been vigorously studied recently for the purpose of solving these problems. One type of resin piquing attention as a biodegradable polymer is a polyhydroxycarboxylic acid polymer. These polymers become, unlike general plastics, totally degraded with ease and eventually converted into water & carbon dioxide.

[0004]

Due to their low combustion calories, furthermore, they do not damage furnaces even in cases where they are incinerated, whereas another characteristic lies in the generation of no harmful gas at the time of combustion. Since easy-to-recycle vegetative resources can be used as feed materials, increasingly depleted petroleum resources can be conserved. They are expected to replace general-purpose resins by virtue of these advantages.

[0005]

Polymers of polyhydroxycarboxylic acids are biodegradable & moldable, and above all, polylactic acid & polyhydroxy butyrate are highly practical. They are,

however, each plagued with such problems as brittleness, inferior processibility, etc., and accordingly, their industrial applications have been limited. It is, in particular, being desired to ameliorate the brittleness of polylactic acid in a state where the transparency thereof is being preserved.

[0006]

Various investigations have been conducted for the purpose of ameliorating the brittleness of polylactic acid, and above all, the addition of a plasticizer has, since early days, been known & investigated as a general polymer modification method. Films or sheets obtained by processing papers or synthetic resins, aluminum foils, etc. have, in the prior art, been used as materials for packaging or storing various liquids, granules & powders, and/or other solids such as foods, beverages, chemicals, non-durable consumer goods, etc. Films or sheets, in particular, bear such excellent characteristics as water resistance, transparency, strength, thermal moldability, low cost, etc. and are therefore being used for many purposes either as bags or cases for packaging or storage applications or, by means of thermal molding, as light-weight containers. Important performance requirements for these packaging or storage materials include thermal melt adhesion friendliness & heat resistance.

[0007]

Films or sheets constituted by synthetic resins are processed into various bags or cases in states where they are

being folded and where one or more sides thereof are being adhered based on the thermal melt adhesion potential of the resin. Such films or sheets, furthermore, are molded, by means of such thermal molding methods as vacuum molding, vacuum compressed air molding, hot panel compressed air molding, deep draw vacuum molding, etc., into light-weight containers for packaging, in rigid manners, such contents as foods, beverages, chemicals, non-durable consumer goods, etc.

[0008]

More often than not, these containers are used after contents have been inserted therein and after the openings thereof have been adhered & sealed with films or sheets or matching lids obtained by thermally molding the former, whereas on these occasions, too, thermal melt adhesion is used. Synthetic resin films or sheets have thus been variously processed by virtue of the thermal melt adhesion potentials thereof and used for practical applications, whereas attributes emphasized on these occasions include the adhesion power of a thermally adhered portion, namely sealing strength, and the physical appearance of the same.

[0009]

These containers, films, and/or sheets, furthermore, are normally required to meet a heat resistance of at least 60°C in consideration of heat resistance requirements during

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storage & transportation, and furthermore, light-weight containers for filling heated contents such as freshly cooked

foods, etc. (e.g., food packs for easy-packing such foods as steamed rice, fried goods, etc., gourmet food containers, & hot-fill containers used for packaging jams, puddings, jellies, etc.) are required to meet not only a heat resistance of at least 80°C but, for the purpose of sealing filled contents, a thermal melt adhesion potential.

[0010]

For the purpose of solving these heat resistance-related problems, U.S. Patent No. 5,076,983 Gazette discloses a method for improving heat resistance wherein a stretched film of polylactic acid is heat-set at 130°C for 1 min. in such a way to lower the shrinkage thereof in a 1-min. boiling water heating test from 66% to 4%, although this film cannot be heat-sealed since it has already been crystallized, whereas such a film comprising of polylactic acid is hard as it is, which is problematic in that its practical applications often become difficult.

[0011]

Japanese Patent Application Publication Kokai No. Hei 10[1998]-151715 Gazette, furthermore, notes that a lactic acid-type polymer laminate using, as the respective constituent materials of a substrate layer & a heat seal layer, either polylactic acid or a lactic acid-type polyester copolymer obtained by copolymerizing a lactic acid component with a polyester component bears a heat resistance of at least 60°C & an excellent sealing strength and can be thermally melt-adhered. A material that uses polylactic acid

as the substrate layer thereof, however, is flawed since it is hard & brittle, whereas a material that uses a lactic acid-type polyester as the substrate layer thereof entails, in a case where it has yet to be stretched, an insufficient impact strength & flexibility and, in a case where it has been stretched, a conspicuous bleedout, and thus, their practical applications are difficult & problematic.

[0012]

(Problems to be solved by the invention)

The present invention attempts to solve these problems by providing a heat seal film endowed with an excellent impact resistance, flexibility, heat resistance, & sealing strength as well as a low bleedout tendency, above all a heat seal film comprising of a yet-to-be-stretched film or sheet bearing an excellent impact resistance, flexibility, heat resistance, & sealing strength and/or a heat seal film comprising of a stretched film or sheet bearing an excellent impact resistance, flexibility, heat resistance, & sealing strength as well as a low bleedout tendency.

[0013]

(Mechanism for solving the problems)

The present inventors compiled intensive investigations for the purpose of solving the aforementioned problems, as a result of which the present invention has been completed after it had been discovered that, in a case where (A): A

crystallized lactic acid-type polyester composition bearing a melting point of at least 120°C and inclusive of polylactic acid & a lactic acid-type polyester is used as a substrate layer and where (B): Either a non-crystalline polylactic acid bearing a softening point of 40 ~ 110°C or a non-crystalline lactic acid-type polyester composition bearing a softening point of 40 ~ 110°C and inclusive of polylactic acid & a lactic acid-type polyester is used as a heat seal layer, it becomes possible to not only to achieve an excellent heat resistance & sealing strength but also to provide a yet-to-be-stretched film or sheet bearing an excellent impact resistance & flexibility and/or a stretched film or sheet bearing a low bleedout tendency.

[0014]

In other words, the present invention provides a heat seal film which is a heat seal film constituted by a substrate layer & a heat seal layer and which is characterized by the facts that the aforementioned substrate layer is comprised of (A): A crystallized lactic acid-type polyester composition bearing a melting point of 120°C or above and inclusive of polylactic acid & a lactic acid-type polyester and that the aforementioned heat seal layer is comprised of (B): Either a non-crystalline polylactic acid bearing a softening point of 40 ~ 110°C or a non-crystalline lactic acid-type polyester composition bearing a softening point of 40 ~ 110°C and inclusive of polylactic acid & a lactic acid-type polyester.

[0015]

(Application embodiments of the invention)

The substrate layer used in the present invention is a layer for realizing a favorable heat resistance and favorable physical properties such as impact resistance & flexibility, and it is comprised of a crystallized lactic acid-type polyester composition {hereafter referred to as the "lactic acid-type polyester composition (A)"} bearing a melting point of 120°C or above and inclusive of polylactic acid & a lactic acid-type polyester {hereafter referred to as the "lactic acid-type polyester (A1)"}.

[0016]

The lactic acid-type polyester composition (A) used in the present invention is a crystallized lactic acid-type polyester composition bearing a melting point of at least 120°C, preferably 120 ~ 300°C, for the purpose of achieving a favorable heat resistance & thermal moldability. A lactic acid-type polyester composition suitable for achieving this objective is a composition wherein the ratio, within the lactic acid units of the polylactic acid or lactic acid-type polyester (A1) included as a constituent component of said lactic acid-type polyester composition, of the optical isomer L form to the D form (L/D ratio) or of the D form to the L form (D/L ratio) is confined to a range of 100/0 ~ 97/3 (mass equivalent). A polylactic acid or lactic acid-type polyester (A1) bearing such a D/L ratio or L/D ratio may, for example,

be obtained & manufactured based on the manufacturing method discussed later by using a lactic acid component bearing the aforementioned D/L ratio or L/D ratio.

[0017]

For the purpose of achieving a favorable impact resistance & flexibility, furthermore, a polymer inclusive of lactic acid units & polyester units within a weight ratio range of 10 : 90 ~ 90 : 10 and bearing a weight-based average molecular weight of at least 10,000 & a glass transition point of 60°C or below is used as the lactic acid-type polyester (A1) of the present invention.

[0018]

The heat seal layer used in the present invention, on the other hand, is a layer to be thermally melt-adhered by means of heat seal, etc. and is comprised of either a non-crystalline polylactic acid bearing a softening point of 40 ~ 110°C or a non-crystalline lactic acid-type polyester composition {hereafter referred to simply as the "lactic acid-type polyester (B)"} bearing a softening point of 40 ~ 110°C and inclusive of polylactic acid & a lactic acid-type polyester {hereafter referred to simply as the "lactic acid-type polyester (B1)"}.

No melting point peak, however, is acknowledged on the "non-crystalline polylactic acid" or "non-crystalline lactic acid-type polyester composition" as it is referred to in the present invention based on the measurement method stipulated by JIS-K-7121.

[0019]

As the non-crystalline polylactic acid or lactic acid-type polyester composition (B) inclusive of polylactic acid & lactic acid-type polyester (B1) used for the heat seal layer,

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one bearing a softening point of 40 ~ 110°C, preferably 40 ~ 100°C, is used for realizing thermal melt adhesion. A polylactic acid or lactic acid-type polyester composition (B) suitable for achieving this objective is a polylactic acid or lactic acid-type polyester (B1) wherein the L form to the D form ratio (L/D ratio) of the lactic acid components thereof is confined to a range of 96/4 ~ 4/96 (mass equivalent). A polylactic acid or lactic acid-type polyester (B1) bearing such an L/D ratio may, for example, be obtained & manufactured based on the manufacturing method discussed below by using, as a feed material, a lactic acid component bearing said L/D ratio.

[0020]

It is desirable, in consideration of the balance of both the heat resistance & sealability performances of the heat seal film of the present invention, for the temperature differential between the melting point of the lactic acid-type polyester composition (A) used for the substrate layer and the melting point of the polylactic acid or lactic acid-type polyester composition (B) used as the heat seal layer on this occasion to be at least 20°C.

[0021]

For the purpose of achieving a favorable impact resistance & flexibility, furthermore, a polymer inclusive of lactic acid units & polyester units within a weight ratio range of 10 : 90 ~ 90 : 10 and bearing a weight-based average molecular weight of at least 10,000 & a glass transition point of 60°C or below is likewise used as the lactic acid-type polyester (B1) of the present invention.

[0022]

It becomes possible to confer an excellent impact resistance & flexibility by adding, to polylactic acid, the above-mentioned lactic acid-type polyester (A1) & lactic acid-type polyester (B1) {the lactic acid-type polyester (A1) & lactic acid-type polyester (B1) may hereafter be referred to simply as "lactic acid-type polyesters" in cases where there exists no need to distinguish them}, and furthermore, they are used as additives capable of inhibiting bleedout in cases where they are added to polylactic acid.

[0023]

At this juncture, the method for manufacturing the lactic acid-type polyester used in the present invention will be explained. Said lactic acid-type polyester is a reaction product obtained by reacting a lactic acid component (a) with a polyester component (b) comprising of a dicarboxylic acid (c) & a diol (d) within a mass ratio range of 10 : 90 ~ 90 : 10.

[0024]

The "lactic acid unit (a')" within the lactic acid-type polyester used in the present invention signifies a chemical structural unit comprising of the lactic acid component (a), whereas the polyester unit (b') likewise signifies a chemical structural unit comprising of the polyester component (b) comprising of the dicarboxylic acid (c) & diol (d).

[0025]

The lactic acid-type polyester (A1) used in the present invention can be obtained by selecting, as will be discussed below, types of the dicarboxylic acid (c) & diol (c) and by adjusting the utilization ratios & reaction conditions of the same in such a way to yield a weight-based average molecular weight of at least 10,000 and a glass transition point of 60°C or below.

[0026]

It is desirable for the utilization ratio, as weight ratio, of the lactic acid component (a) & polyester component (b) to be confined to a range of 90 : 10 ~ 10 : 90, whereas a range of 40 : 60 ~ 90 : 10 is more desirable, whereas a range of 50 : 50 ~ 90 : 10 is even more desirable, whereas a range of 50 : 50 ~ 85 : 15 is especially desirable.

[0027]

Lactic acid components (a) are instantiated by lactic acid, lactides, polylactic acid, & polylactides. Lactides are compounds obtained as a result of cyclic dimerization of two lactic acid molecules, and they are monomers encompassing

stereoisomers instantiated by L-lactide comprising of two L-lactic acid molecules, D-lactide comprising of two D-lactic acid molecules, and meso-lactide comprising of D-lactic acid & L-lactic acid.

[0028]

A copolymer inclusive of L-lactide or D-lactide alone becomes crystallized and bears a high melting point. A lactic acid-type polyester to be used for the substrate layer or heat seal layer can therefore be provided by combining the these three types of lactides at the above-mentioned ratio depending on applications.

[0029]

Commercial products of L-lactic acid or D-lactic acid are generally available as aqueous solutions of 80 ~ 90%. As far as the present invention is concerned, commercially sold aqueous lactic acid solutions can be directly used. As in the case of lactides, various physical properties (e.g., melting point, melt viscosity, etc.) of the lactic acid-type polyester can be adjusted by varying the compositional ratio of L- & D-lactic acids.

[0030]

On this occasion, it is desirable to use polylactic acid or lactide as the lactic acid component (a). The reason is because the lactic acid-type polyester obtained in a case where said polylactic acid or lactide is used as a feed material is a block copolymer capable of effectively maintaining transparency and/or of improving the bleedout

inhibitory function and of conferring an excellent impact resistance.

[0031]

The polyester component (b) used in the present invention is obtained by esterifying the dicarboxylic acid (c) & diol (d).

[0032]

Such dicarboxylic acids (c) may, for example, be instantiated by dicarboxylic acids in possession of 4 ~ 45 carbon atoms, namely aliphatic dicarboxylic acids such as succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, decanedicarboxylic acid, cyclohexanedicarboxylic acid, dimeric acid, etc.; unsaturated aliphatic dicarboxylic acids such as fumaric acid, etc.; aromatic dicarboxylic acids such as phthalic acid, terephthalic acid, isophthalic acid, naphthalenedicarboxylic acid, etc.; etc. The dicarboxylic acids (c), however, are not limited to these examples. Two or more types of these dicarboxylic acids may, furthermore, be used in combination.

[0033]

Especially desirable examples of these dicarboxylic acids (c) are dicarboxylic acids in possession of 4 ~ 12 carbon atoms & optionally inclusive of unsaturated bonds and dicarboxylic acids in possession of 20 ~ 45 carbon atoms & optionally inclusive of unsaturated bonds such as succinic acid, adipic acid, sebacic acid, decanedicarboxylic acid,

cyclohexanedicarboxylic acid, dimeric acid, phthalic acid, terephthalic acid, isophthalic acid, dimeric acid or hydrogenated dimeric acid, etc. Above all, a lactic acid-type polyester composition comprising of a lactic acid-type polyester using a dimeric acid in possession

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of 20 ~ 45 carbon atoms provides a polyester composition bearing an excellent transparency and an excellent impact resistance, and therefore, dimeric acids in possession of 20 ~ 45 carbon atoms may be cited as especially desirable examples.

[0034]

There are no special restrictions on dimeric acids to be used so long as they are dicarboxylic acids in possession of at least 24 carbon atoms and generated as a result of thermal dimerizing reactions, etc. of unsaturated fatty acids in possession of at least 12 carbon atoms, although it is desirable for the toxicities of oleic acid or tall oil fatty acids used as feed materials to be low. Various reaction mechanisms have been proposed for thermal dimerizing reactions, whereas a dimeric acid inclusive of an intramolecular alicyclic structure predicated presumably on a thermal Diels-Alder cyclizing reaction as a main mechanism is especially desirable to use in the present invention.

[0035]

Such dimeric acids are classified into ones in possession of intramolecular unsaturated double bonds and

fatty acids saturated by means of hydrogenation, and both unsaturated & saturated dimeric acids are usable.

[0036]

Commercial products of dimeric acids are instantiated by dimers of aliphatic unsaturated carboxylic acids in possession of 18 carbon atoms (Enpol 1061 & 1062 manufactured by Cognis Co.), dimers of aliphatic saturated carboxylic acids in possession of 18 carbon atoms (Enpol 1008, etc. manufactured by the same company), etc. These commercially sold dimeric acids often include some monomeric acids & trimeric acids, and these dimeric acids are also permissible. It is desirable for the purity of the dimeric acid to be at least 90%, preferably at least 95%. It is desirable for any of these dimeric acid components to be a non-toxic one permitted to be used for food packaging materials.

[0037]

It is desirable for the utilization ratio of the dicarboxylic acid (c) with respect to 100 parts by weight of the lactic acid-type polyester component to be at least 10 parts by weight, preferably at least 30 parts by weight. Incidentally, a polyester that uses an aromatic dicarboxylic acid tends to entail a high glass transition point (T_g), and therefore, in a case where an aromatic dicarboxylic acid is used, it is desirable to select types & quantitative ratios of materials in such a way not to adversely affect the effects of conferring impact resistance & flexibility. It is desirable for the ratio of aliphatic dicarboxylic acid(s)

with respect to the total sum of the dicarboxylic acid (c) to be confined to a range of 30 ~ 100 wt%.

[0038]

Diols (d), on the other hand, may, for example, be instantiated by ethylene glycol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,7-heptanediol, 1,8-octanediol, 1,9-nonanediol, 1,10-decanediol, 1,11-undecanediol, 1,12-dodecanediol, 1,4-cyclohexanedimethanol, propylene glycol, 1,3-butanediol, 1,2-butanediol, neopentyl glycol, 3,3-diethyl-1,3-propanediol,

[0039]

3,3-dibutyl-1,3-propanediol, 1,2-butanediol, 1,2-pentanediol, 1,3-pentanediol, 2,3-pentanediol, 2,4-pentanediol, 2-methyl-2,4-pentanediol, 1,4-pentanediol, 1,2-hexanediol, 1,3-hexanediol,

[0040]

1,4-hexanediol, 1,5-hexanediol, n-butoxyethylene glycol cyclohexanedimethanol, hydrogenated bisphenol A, dimer diol, diethylene glycol, dipropylene glycol, triethylene glycol, polyethylene glycol, polypropylene glycol, polytetramethylene glycol, xylylene glycol, phenylethylene glycol, and other aliphatic diols in possession of 2 ~ 45 carbon atoms. These diols may also be used in combination of two or more types.

[0041]

Of these diols, aliphatic diols in possession of 2 ~ 45 carbon atoms & optionally inclusive of unsaturated bonds are desirable, and above all, aliphatic diols in possession of 2

~ 12 carbon atoms & optionally inclusive of unsaturated bonds and/or aliphatic diols in possession of 20 ~ 45 carbon atoms & optionally inclusive of unsaturated bonds are especially desirable. Of these, furthermore, in a case where a lactic acid-type polyester derived from a polyester component using a dimer diol in possession of 20 ~ 45 carbon atoms is added to polylactic acid, it is especially desirable in that it becomes possible to provide a polyester composition bearing an excellent transparency and an excellent impact resistance.

[0042]

The dimer diol is a diol obtained by reducing dimeric acid, and as such, ones in possession of 20 ~ 45 carbon atoms are desirable, and above all, the reduction product of the dimer of an aliphatic unsaturated carboxylic acid in possession of 18 carbon atoms, a dimer diol in possession of 36 carbon atoms, etc. are especially desirable. It is desirable for the purity of the dimer diol to be at least 90%, preferably at least 95%. Either the dimeric acid or dimer diol may be used alone, although both may be safely used together. An example of commercial products of dimer diols is a dimer diol in possession of 36 carbon atoms obtained by reducing the dimer of an aliphatic unsaturated carboxylic acid in possession of 18 carbon atoms (manufactured by Toa Gosei Chemical Co.).

[0043]

It is desirable for the ratio of the aliphatic diol(s) with respect to the total sum of diols (d) to be confined to

a range of 30 ~ 100 wt%, whereas it is desirable for the utilization ratio of the diol (d) with respect to 100 parts by weight of the lactic acid-type polyester component to be at least 10 parts by weight, preferably at least 30 parts by weight.

[0044]

Both liquid & solid ones are known as polyesters (b), whereas the melting point & fluidization point of the same become lower as the constituent ratios of dimeric acid, dimmer diol, propylene glycol, and/or 1,3-butanediol in possession of side chains become higher. A lactic acid-type polyester derived from a polyester (b) comprising of such

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components therefore bears a low elasticity and is desirable in that it is capable of conferring especially favorable impact resistance & flexibility onto the polylactic acid.

[0045]

There are no special restrictions on the weight-based average molecular weight of the polyester component (b) obtained by esterifying the dicarboxylic acid (c) & diol (d), although a value of 2,000 or higher is desirable, whereas a value of 5,000 or higher is more desirable, whereas a range of 10,000 ~ 200,000 is more desirable, whereas a range of 20,000 ~ 150,000 is even more desirable, whereas a range of 20,000 ~ 100,000 is especially desirable.

[0046]

A high-molecular-weight polyester (b) with a molecular weight of at least 100,000 can be manufactured by reacting, as a chain extending agent, an acid anhydride or polyisocyanate with a polyester obtained by esterifying the dicarboxylic acid (c) & diol (d). The polyester component (e) [sic: Presumably "(b)"?] used in the present invention encompasses such a polyisocyanate-modified polyester obtained by using a polyisocyanate as a chain extending agent.

[0047]

As far as the method for manufacturing the polyester (b) is concerned, the dicarboxylic acid (c) & diol (d) are agitated at a molar ratio of 1 : 1 ~ 1 : 1.5 within a nitrogen atmosphere in a state where the temperature is being gradually elevated within a range of 130°C ~ 240°C at a rate of 5 ~ 10°C per hour and where water is being distilled & removed. After the reaction has been induced for 4 ~ 12 hours, an excess of diol is distilled & removed in a state where the magnitude of vacuum is being gradually upped within a range of 90 ~ 0.1 KPa. After this vacuum has been maintained for 2 ~ 3 hours, a transesterification catalyst & an antioxidant are added, and the contents are reacted at 200 ~ 240°C for 4 ~ 12 hours in a state where the magnitude of vacuum is being maintained at 0.5 KPa or below, as a result of which a polyester (b) bearing a high viscosity can be obtained.

[0048]

From the standpoint of mitigating coloration problematic in the course of the transesterifying reaction, a method wherein a transesterifying reaction is induced by using 10 ~ 1,000 ppm of a metal catalyst (e.g., Ti, Sn, Zn, Mg, Al, Zr, Hf, etc.) with respect to the polyester and wherein 10 ~ 1,000 ppm of an antioxidant (e.g., phosphorous acid ester compound, etc.) is further added is desirable.

[0049]

Metal catalysts may, for example, be instantiated by titanium tetraisopropoxide, titanium tetrabutoxide, titanium oxyacetylacetonate, tin octanate, tin 2-ethylhexanate, zinc acetylacetonate, zinc acetate, magnesium acetate, zirconium tetrachloride, hafnium tetrachloride, hafnium tetrachloride-THF complex, etc.

[0050]

It is also possible, for the purpose of conferring a more favorable impact resistance, to elevate the molecular weight of the polyester obtained by the above-mentioned manufacturing method or, for the purpose of lowering the melt viscosity, to branch said polyester.

[0051]

The molecular weight of the polyester can be elevated by reacting said polyester with an acid anhydride or polyvalent isocyanate, etc. based on a publicly known method of the prior art. In other words, a high-molecular-weight polyester (b) can be manufactured by adding an acid anhydride or

polyvalent isocyanate to a polyester within a temperature range of 180°C ~ 210°C and by reacting the obtained mixture for 3 hours within a vacuum range of 0.5 ~ 0.1 KPa in the case of the carboxylic anhydride or at normal pressure in the case of the polyvalent isocyanate.

[0052]

Carboxylic anhydrides of compounds in possession of at least two intramolecular carboxyl groups are conceivable as the above-mentioned acid anhydrides. Such carboxylic anhydrides may, for example, be instantiated by succinic anhydride, cyclohexanedicarboxylic anhydride, phthalic anhydride, maleic anhydride, trimellitic anhydride, pyromellitic dianhydride, etc. Two or more types of these carboxylic anhydrides may also be used in combination.

[0053]

The polyvalent isocyanate used for upping the molecular weight of the polyester is a compound in possession of at least two intramolecular isocyanato groups. It is desirable to use a bifunctional compound in a case where a urethane bond-containing polyester bearing a virtually linear structure is targeted as the objective product.

[0054]

The above-mentioned bifunctional isocyanates may, for example, be instantiated by hexamethylene diisocyanate, 2,4-toluylene diisocyanate, 2,5-toluylene diisocyanate, toluene diisocyanate, xylylene diisocyanate, diphenylmethane diisocyanate, 1,5-naphthylene diisocyanate, isophorone

diisocyanate, hydrogenated diphenylmethane diisocyanate, etc. Two or more types of these bifunctional isocyanates may also be used in combination.

[0055]

For the purpose of branching the polyester, furthermore, it is also possible to react a trifunctional or higher polyvalent isocyanate based on a publicly known method of the prior art. In this case, a starry polymer chain becomes obtained. Compounds used for obtaining such a structure are instantiated by compounds obtained by modifying polyvalent alcohols with bifunctional isocyanates, which are represented by a pentaerythritol modified with a bifunctional isocyanate. As said polyvalent isocyanate, several types of polyvalent alcohols may also be used in combination, whereas the goal of upping the molecular weight without entailing gelation can be achieved by using a small quantity of a trifunctional or higher isocyanate(s) in combination with a bifunctional isocyanate.

[0056]

The reaction of the polyester with the carboxylic anhydride or polyvalent isocyanate may be induced based on a method wherein a carboxylic anhydride or polyvalent isocyanate is mixed with a reaction product prevailing immediately after the completion of the ester polymerizing reaction of the diol (c) & dicarboxylic acid (d) [sic: Presumably "diol (d) & dicarboxylic acid (c)"] and wherein the contents are then agitated & reacted in a molten state

over a brief period or a method wherein the same is added anew to a polyester obtained as a result of polymerization and wherein the contents are then melted & mixed.

[0057]

In a case where the polyvalent isocyanate is used, a method wherein both a polyester & an isocyanate are solubilized into a common solvent and then heated & reacted is especially desirable. It becomes possible, according to such a method, to disperse the polyisocyanate within the aliphatic polyester in an extremely homogeneous fashion. The temperature at which the acid anhydride or polyvalent isocyanate is mixed & reacted

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with the polyester is normally 70°C ~ 220°C, preferably 100°C ~ 190°C.

[0058]

It is desirable to use, on an occasion where the polyvalent isocyanate is reacted, to use ester polymerization catalysts (e.g., N,N-dimethylaniline, tin octanate, tin 2-ethylhexanate, dibutyltin dilaurate, tetraisopropyl titanate, etc.) or urethane catalysts. It is desirable for the utilization ratio of the acid anhydride and/or polyvalent isocyanate with respect to the polyester (II') to be confined to a range of 0.01 wt% ~ 5 wt%, preferably 0.1 wt% ~ 1 wt%.

[0059]

In a case where oxygen migrates into the reaction system on an occasion for synthesizing a polyester, it may

contribute to coloration & decomposition as well as, in a case where a feed material in possession of an unsaturated bond is used, to gelation, and therefore, it is desirable for the atmosphere to be sufficiently substituted with an inert gas (e.g., nitrogen, etc.) on an occasion where the vacuum established for the addition of a catalyst, etc. becomes canceled.

[0060]

It is desirable for the weight-based average molecular weight of the lactic acid-type polyester used in the present invention to be at least 10,000. From the standpoint of conferring an excellent impact resistance in a state where the transparency is being maintained and/or where the effect of inhibiting bleedout is being improved, furthermore, it is desirable for the weight-based average molecular weight of the same to be confined to a range of 20,000 ~ 200,000, whereas a range of 30,000 ~ 200,000 is more desirable, whereas a range of 40,000 ~ 150,000 is especially desirable.

[0061]

In a case where said weight-based average molecular weight is at least 10,000, it is desirable in that it becomes possible to confer a sufficient plasticizing effect & impact strength without entailing the transparency loss of the resin composition. The upper limit of the molecular weight, on the other hand, is not particularly limited, although the limit is generally 200,000 or below, and 150,000 or below is desirable in consideration of utility friendliness.

[0062]

It is desirable for the glass transition point (T_g) of the lactic acid-type polyester to be confined to a range of $-70^{\circ}\text{C} \sim 60^{\circ}\text{C}$, whereas a range of $-65^{\circ}\text{C} \sim 60^{\circ}\text{C}$ is especially desirable. The storage modulus (E'), at 20°C , of the lactic acid-type polyester (A1) and/or lactic acid-type polyester (B1) of the present invention, wherein the weight-based average molecular weights & glass transition points thereof are designed respectively to be at least 10,000 & 60°C or below, is 2.5 GPa or below, preferably $0.1 \sim 2.0$ GPa.

[0063]

Concrete methods for manufacturing the lactic acid-type polyester (A1) or (B1) of the present invention may, for example, be instantiated by (1): A method wherein a lactide is reacted with a polyester component (b) in the presence of a polymerization catalyst; (2): A method wherein polylactic acid is obtained by polycondensing lactic acid and wherein said polylactic acid is further dehydrated & polycondensed in the presence of a polyester component (b) for obtaining a polylactic acid-polyester block copolymer; (3): A method wherein a polylactic acid-polyester block copolymer is obtained by melt-kneading a polylactic acid obtained from lactic acid or lactide with a polyester component (b) in the presence of a transesterification catalyst; etc.

[0064]

First, the method for copolymerizing the lactide & polyester component (b) of (1) will be explained. It is

desirable, from the standpoint of preventing the coloration & decomposition of the lactide, for the reaction temperature to be 220°C or below, more preferably 200°C or below, or most preferably 180°C or below, whereas it is desirable, from the standpoint of preventing the coloration & decomposition of the lactide, for the reaction to be induced within an inert gas (e.g., nitrogen, argon, etc.) atmosphere. Moreover, since the existence of water within the reaction system is undesirable, it is necessary to sufficiently dry the aliphatic polyester.

[0065]

The polyester (b) & lactide are mutually mixed & solubilized at 100°C ~ 220°C under such conditions. On this occasion, it is also possible, if necessary, to use 1 ~ 30 parts by weight, more preferably 5 ~ 30 parts by weight, or most preferably 15 ~ 30 parts by weight, of an inert solvent (e.g., toluene, etc.) with respect to [100 parts by weight of?] their combined sum. Moreover, 50 ~ 2,000 ppm of a polymerization catalyst (e.g., tin octanate, etc.) is added with respect to the combined sum of the polyester (b) & lactide within an inert gas (e.g., nitrogen, argon, etc.) atmosphere at 140 ~ 220°C. As far as the feeding ratio of the polyester (b) & lactide is concerned, it is desirable for the weight ratio thereof to satisfy polyester (b) : lactide = 10 : 90 ~ 90 : 10, more preferably 40 : 60 ~ 90 : 10, even more preferably 50 : 50 ~ 90 : 10, and most preferably 50 : 50 ~ 85 : 15.

[0066]

All catalysts generally known as esterification catalysts & decyclizing polymerization catalysts are usable as said polymerization catalysts, and they may, for example, be instantiated by alkoxides, acetates, oxides, chlorides, etc. of Sn, Ti, Zr, Zn, Ge, Co, Fe, Al, Mn, Hf, etc. Of these, a tin powder, tin octylate, tin 2-ethylhexylate, dibutyltin dilaurate, tetraisopropyl titanate, tetrabutoxytitanium, titanium oxyacetylacetonate, iron (III) acetylacetonate, iron (III) ethoxide, aluminum isopropoxide, & aluminum acetylacetonate are desirable in that they are capable of accelerating reactions.

[0067]

Next, the method for copolymerizing lactic acid & polyester (b) of (2) will be explained. A lactic acid-type polyester can be obtained by polycondensing lactic acid based on a publicly known & routinely practiced method, by adding the polyester (b) to the obtained polylactic acid, and by further polycondensing the obtained mixture. Various techniques for polycondensing lactic acid have been disclosed, and the polylactic acid obtained by any of these methods suffices. As far as the present invention is concerned, effects of conferring impact resistance & flexibility are acknowledged so long as the molecular weight of the lactic acid-type polyester is at least 10,000, and therefore, the feeding ratio of the lactic acid component (a) & polyester component (b) and the terminal group number or

molecular weight of the polyester (b) may be adventitiously adjusted in consideration of the targeted molecular weight of the lactic acid-type polyester. Incidentally, a higher molecular weight of the polylactic acid is desirable in that a high-molecular-weight lactic acid-type polyester can be obtained as a result of a brief copolymerizing reaction after the addition of the polyester (b).

[0068]

As a method for further upping the molecular weight of the polylactic acid, furthermore, it is also possible to use a solvent at the time of polycondensing lactic acid,

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and it is possible to facilitate the progress of polymerization by selecting a high-boiling-point solvent which tends to form an azeotropic mixture with water (e.g., toluene, xylene, anisole, diphenyl ether, etc.), by forming an azeotropic mixture of said solvent & water, by dehydrating said mixture by using a desiccant, etc. and/or distillation, and by returning the solvent to the reaction system once again. In a case where the polymerization catalyst cited earlier (e.g., tin powder, etc.) is used on this occasion, it is especially desirable since the duration of the reaction can be abbreviated.

[0069]

On an occasion for facilitating the progress of polycondensation by heating a mixture of the polylactic acid obtained as a result of the polycondensation of lactic acid

and the polyester (b), it is also possible to further add a diol or dicarboxylic acid for the purpose of adjusting the ratio of terminal groups with respect to the fed quantitative ratio. As far as reaction conditions on this polycondensation occasion are concerned, it is desirable for the reaction to be induced at 220°C or below from the standpoint of preventing the decomposition & coloration of the lactic acid block, whereas it is desirable, from the standpoint of further upping the molecular weight, to lower the pressure to 1 KPa or below by adding the polymerization catalyst(s) cited earlier (e.g., tin powder, tin octanate, etc.). In a case where an azeotropic dehydrating polycondensation reaction is induced by using a solvent similar to that used at the time of the polycondensation of lactic acid, furthermore, it is especially desirable in that a lactic acid-type polyester of a higher molecular weight can be obtained.

[0070]

Next, the method of (3), wherein a polylactic acid-polyester block copolymer is obtained by melt-kneading, in the presence of a transesterification catalyst, the polylactic acid derived from lactic acid or lactide and the polyester (b), will be explained. The polylactic acid & polyester (b) are mutually mixed, heated, & transesterified in the presence of the polymerization catalyst cited earlier (e.g., tin octanate, etc.). As far as reaction conditions are concerned, it is desirable, from the standpoint of

preventing the decomposition & coloration of the lactic acid block, for the reaction to be induced at 220°C or below, and furthermore, it is desirable for the reaction to be induced within an inert gas (e.g., nitrogen, argon, etc.) atmosphere. The polylactic acid may, furthermore, be obtained from either lactic acid or lactide, whereas a higher polylactic acid molecular weight is desirable from the standpoint of obtaining a high-molecular-weight lactic acid-type polyester, and it is desirable for the molecular weight of the polylactic acid in terms of the weight-based average molecular weight thereof to be at least 50,000, more preferably at least 100,000, or most preferably at least 150,000.

[0071]

The lactide, furthermore, is soluble with various solvents and may therefore be subjected to each of the above-mentioned manufacturing methods after having been solubilized into a solvent (e.g., toluene, benzene, xylene, ethylbenzene, tetrahydrofuran, dioxane, diphenyl ether, chlorobenzene, etc.). Incidentally, it is desirable for the hydroxyl group(s) or carboxyl group(s) at either or both terminals of the lactic acid-type polyester used in the present invention to be capped with a carboxylic acid or alcohol. The reason is because the hydroxyl group or carboxylic acid [sic: Presumably "carboxyl group"] of the lactic acid-type polyester may entail a matrix polymer molecular weight loss on a blending occasion, and the capping of the terminal(s) of

said lactic acid-type polyester is effective for preventing this molecular weight loss. In a case where a lactic acid-type polyester with a molecular weight of 10,000 or below is used, in particular, the number of terminal groups is large, and it is therefore desirable to cap the terminal(s) thereof.

[0072]

Moreover, the preservation stability of the lactic acid-type polyester can be further improved by extracting & removing, by using a solvent, the polymerization catalyst or by deactivating the polymerization catalyst with a catalyst deactivating agent after the copolymerization of the lactic acid-type polyester.

[0073]

The residual polymerization catalyst within the polylactic acid or lactic acid-type polyester may accelerate decomposition due to a reversible reaction on the melt-kneading occasion, and therefore, it is desirable to remove or deactivate the polymerization catalyst used for manufacturing the same for the purpose of preventing such an inconvenience.

[0074]

Concrete methods for removing polymerization catalysts are instantiated by a method wherein a resin pellet of the lactic acid-type polyester is immersed within an aqueous methanol/hydrochloric acid solution, aqueous acetone/hydrochloric acid solution, or corresponding mixed solution and a method wherein a lactic acid-type polyester

abiding in a solution state is mixed with the aforementioned solution and wherein a polymer being precipitated is washed. It becomes possible, according to such methods, to simultaneously wash away & remove traces of residual monomers, oligomers, etc.

[0075]

It is also possible to deactivate the polymerization catalyst by adding a catalyst deactivating agent during or after the manufacture of the lactic acid-type polyester. The catalyst deactivating agent normally becomes adhered to the polymerization catalyst within the lactic acid-type polyester in a quasi-chelated morphology and included within the lactic acid-type polyester, whereas it may be subsequently removed by means of solvent washing, etc.

[0076]

The optimal addition ratio of the catalyst deactivating agent differs depending on types of catalysts used on an occasion for manufacturing the lactic acid-type polyester as well as on reaction conditions, although a quantitative ratio at which the concomitantly used polymerization catalyst can be deactivated suffices, and 0.001 ~ 10 parts by weight, more preferably 0.1 ~ 5 parts by weight, or most preferably 0.5 ~ 3 parts by weight, of such an agent is normally added with respect to 1 parts by weight of the concomitantly used catalyst either prior to the retrieval of the polymer upon the completion of the lactic acid-type polyester polymerizing reaction or during a kneading process. It is also possible

to add & knead the catalyst deactivating agent to & with the manufactured lactic acid-type polyester.

[0077]

Chelating agents and/or acidic phosphoric acid esters are especially desirable as catalyst deactivating agents used in the present invention. There are no special restrictions on such chelating agents, although usable ones may, for example, be instantiated by ethylenediaminetetraacetic acid, disodium ethylenediaminetetraacetate, oxalic acid, phosphoric acid, pyrophosphoric acid, alizarin, acetylacetone, diethylenetriaminepentaacetic acid, triethylenetetraminehexaacetic acid, catechol, 4-tert-butylcatechol, L(+)-tartaric acid, DL-tartaric acid, glycine, chromotropic acid, benzoylacetone, citric acid, gallic acid, dimethylcaptopropanol, triethanolamine, cyclohexanediaminetetraacetic acid, ditoluoyltartaric acid, & dibenzoyltertaric acid.

[0078]

The acidic phosphoric acid ester, furthermore, serves, by forming a complex with a metal ion included within a hydroxycarboxylic acid-type polyester, functions of attenuating the catalyst activity and of inhibiting the severance of a polymer chain. The "acidic phosphoric acid ester" encompasses acidic phosphoric acid esters, phosphonic acid esters, alkylphosphonic acid esters, and corresponding mixtures.

[0079]

Acidic phosphoric acid esters may, for example, be instantiated by traditional & publicly known acidic phosphoric acid esters, phosphonic acid esters, alkylphosphonic acids, & corresponding mixtures mentioned in the specification of U.S. Patent No.

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5,686,540. The acidic phosphoric acid ester component ensures, by virtue of excellent solubilities thereof with organic solvents, excellent operative efficiencies, bears an excellent reactivity with the lactic acid-type polyester, and exhibits an excellent polymerization catalyst deactivating effect.

[0080]

With regard to any of the aforementioned methods for manufacturing lactic acid-type polyesters, there are no special restrictions on the polymerization conversion of the copolymerizing reaction, although it is desirable to achieve an eventual polymerization addition ratio [sic: Presumably "polymerization conversion"] of 90 ~ 99% by inducing a reaction at 160 ~ 180°C for at least 1.5 hours, more preferably at least 2.5 hours, or most preferably at least 3 hours, in a state where the polymerization conversion is being measured by means of gel permeation chromatography (GPC).

[0081]

In a case where the lactic acid-type polyester of the present invention is provided by means of decyclizing

copolymerization, it can be manufactured by using an ordinary reaction pot, and a manufacturing apparatus of the CSTR type provided by customizing said pot for continuous production can be used. In a case where a material of a rather high viscosity is involved, the agitation efficiency deteriorates in the course of a copolymerizing reaction within a normal reaction pot, accompanied by coloration & reactivity loss due to local heating. In such a case, it is desirable to use a static mixer capable of homogeneous agitation & accompanied by a minimal shear stress.

[0082]

Moreover, the present reaction can be induced by using a static mixer alone, although a method wherein an ordinary reaction pot is used at a stage where the viscosity is low and wherein a static mixer is used prior to a viscosity gain in the latter half of polymerization is especially desirable from the standpoint of homogeneously mixing a polymerization starter. As far as the viscoelasticity of the lactic acid-type polyester at room temperature is concerned, a softer product becomes obtained as the number of principal chain carbon atoms of the diol constituting the aliphatic polyester used for copolymerization increases. Moreover, a softer product becomes obtained as the quantitative ratio of the dicarboxylic acid used in combination with the dimeric acid increases.

[0083]

Next, the lactic acid-type polyester composition (A) inclusive of polylactic acid & the lactic acid-type polyester (A1) and polylactic acid or lactic acid-type polyester composition (B) inclusive of polylactic acid & the lactic acid-type polyester (B1) used in the present invention {the lactic acid-type polyester composition (A) & lactic acid-type polyester composition (B) may hereafter be referred to simply as "lactic acid-type polyester compositions" in cases where there exists no need to distinguish them}.

[0084]

There are no special restrictions on the weight-based average molecular weight of the polylactic acid used for the lactic acid-type polyester composition of the present invention, although it is generally desirable for said weight-based average molecular weight to be at least 50,000, more preferably at least 70,000, or most preferably at least 100,000, and preferably 500,000 or below.

[0085]

The lactic acid-type polyester used in the present invention may be kneaded with polylactic acid as it is, or it may instead be used as a master batch with which polylactic acid has preliminarily been blended at a high concentration.

[0086]

There are no special restrictions on the mixing ratio between the lactic acid-type polyester & polylactic acid constituting the lactic acid-type polyester composition used in the present invention so long as the effects of the

present invention can be achieved, although it is desirable for said ratio to satisfy lactic acid-type polyester : polylactic acid = 3 : 97 ~ 70 : 30, more preferably 5 : 95 ~ 50 : 50, or most preferably 5 : 95 ~ 40 : 60. In a case where the compositional ratio is confined to this range, it becomes possible to improve the heat resistance, impact resistance, & bleedout resistance of the blend in well-balanced manners.

[0086]

As far as conditions for mixing the lactic acid-type polyester & polylactic acid are concerned, the mixing operation is carried out at or above the melting point of the polylactic acid, although a range of approximately 180 ~ 200°C is desirable since the melting point of the lactic acid-type polyester used in the present invention is 140°C ~ 170°C. In a case where the temperature exceeds 200°C, it becomes necessary to adjust the mixing time, mixing rotation frequency, etc. in anticipation of a polylactic acid molecular weight loss.

[0088]

An extruder, kneader, batch-type mixing machine, etc. can be used as mixing apparatuses. A mixing operation may be carried out within a reaction pot, and, in a case where the viscosity is high, a blending operation may be carried out by using a static mixer. Similar blending effects can be achieved based on a wet blending method that uses a solvent, whereas it is desirable for an operation for evaporating the

solvent to be carried out at a high temperature & at a reduced pressure over a brief period for the purpose of preventing polymer separation.

[0089]

Since the lactic acid-type polyester composition used in the present invention exhibits an excellent impact resistance, it exhibits, in a case where it is used as a substrate layer or heat seal layer, an excellent DuPont impact strength of at least 0.2 J, preferably 0.3 ~ 5 J, as a 250 μm yet-to-be-stretched film or stretched film and an excellent film impact profile of at least 1 J, preferably 1 ~ 10 J, as a stretched & heat set sheet.

[0090]

Since the lactic acid-type polyester composition used in the present invention exhibits an excellent flexibility, furthermore, it exhibits, in a case where it is used as a substrate layer or heat seal layer, an excellent storage modulus (E'), as it is measured in compliance with the JIS-K-7198 method A, within a range of 0.5 ~ 3.0 GPa, preferably 0.6 ~ 2.4 GPa.

[0091]

A lactic acid-type polyester composition obtained by adding, to polylactic acid, the lactic acid-type polyester used in the present invention, furthermore, is capable of perpetuating an excellent transparency. The haze value of a press sheet with a thickness of 250 μm obtained by adding 30 of the lactic acid-type polyester to 100 parts by weight of

polylactic acid, for example, is 35% or below, more preferably 1 ~ 30%, or most preferably 1 ~ 25%.

[0092]

Since the boundaries of films & sheets are not clearly distinguished, however, films & sheets may be referred to collectively as "films" in the present invention.

[0093]

A lactic acid-type polyester composition inclusive of the lactic acid-type polyester used in the present invention exhibits an excellent effect of inhibiting bleedout, and in a case where a 10 × 10 cm square yet-to-be-stretched or stretched sheet with a thickness of 250 μm is left unattended within a thermostat & humidistat vessel at a humidity of 80%, no bleedout occurs on the surface of said molded product for at least 60 days.

[0094]

The polylactic acid or lactic acid-type polyester composition inclusive of the lactic acid-type polyester & polylactic acid used for the substrate layer or heat seal layer of the present invention bears an excellent biodegradability, and even in a case where it is

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discarded within sea water, it becomes decomposed due to hydrolysis, biodegradation, etc. For this reason, the resin can, due to the attenuated strength thereof, be decomposed in sea water within several months to the extent that its original contour is unrecognizable. In a case where a

compost is used together, furthermore, the same can be biodegraded to the extent that the original shape thereof is unrecognizable within an even shorter time, whereas in a case where the same is incinerated, it emits neither toxic gases nor other toxic substances.

[0095]

Next, the heat seal film of the present invention will be explained. There are no special restrictions on the thickness of the heat seal film of the present invention, although a sheet-shaped structure bearing a thickness of 5,000 μm or less in a laminated state is desirable. Likewise, there are no special restrictions on the thickness of the substrate layer, although a range of 5 ~ 3,000 μm is desirable, whereas a range of 5 ~ 200 μm is more desirable in consideration of the strength & economy, and a range of 5 ~ 100 μm is especially desirable. Likewise, there are no special restrictions on the thickness of the heat seal layer, although a range of 1 ~ 30 μm is desirable in consideration of film moldability, whereas a range of 2 ~ 20 μm , preferably 3 ~ 10 μm , is more desirable in consideration of the sealing shrinkage & economy.

[0096]

It is also possible, if necessary, to coat the surface of the heat seal film of the present invention with a second and/or third component(s) selected from among publicly known & routinely used additives such as other polymers, plasticizers, stabilizers, antioxidants, anti-blocking

agents, anti-clouding agents, coloring agents, etc. or to add the same to the resin constituting said film. As said "other polymers," aliphatic polyesters, polyvinyl alcohol, polyhydroxy butyrate-hydroxy valerate, starch-type polymers, etc. may be included.

[0097]

Said additives are instantiated by a polyester-type plasticizer comprising of 1,3-butanediol & adipic acid, other plasticizers such as dioctyl phthalate, polyethylene glycol-adipic acid, etc., stabilizers such as epoxylated soybean oil, carbodiimide, etc., antioxidants such as 2,6-di-tert-butyl-4-methylphenol (BHT), butylhydroxyanisole (BHA), etc., anti-blocking agents such as silica, talc, etc., anti-clouding agents such as glycerin fatty acid esters, monostearyl citrate, etc., and coloring agents such as titanium oxide, carbon black, ultramarine blue, etc.

[0098]

Adhesion methods predicated on thermal melt adhesion are instantiated by the heat sealing method, impulse sealing method, rupture sealing method, impulse rupture sealing method, ultrasonic sealing method, high frequency sealing method, etc., and of these, the heat sealing method, impulse sealing method, & rupture sealing method are used generally & often. The heat seal film of the present invention is provided by laminating the substrate layer & heat seal layer, whereas as a method for laminating the same, a co-extrusion film molding method that uses two or more extruders is the

most practical. It is also possible to use a method wherein a heat seal layer is melt-extruded & laminated onto a preliminarily formed substrate layer, a method wherein preliminarily formed substrate & heat seal layers are mutually laminated via an adhesive, etc.

[0099]

A metal or metal oxide may be deposited on the substrate layer, or said layer may instead be printed or subjected to two or more types of such treatments.

[0100]

Extrusion film molding methods for the substrate layer or heat seal layer as well as concomitantly established conditions will be discussed. Since lactic acid-type polymers generally bear high hygroscopicities & strong hydrolyzing tendencies, they require water content managements, and in a case where a polylactic acid or lactic acid-type polyester is extrusion-molded by using a general monoaxial extruder, it is necessary to dehumidify & dry the same within a vacuum dryer, etc. prior to film molding. A film molding operation that uses a vent-type biaxial extruder is capable of achieving an advanced dehydrating effect, and since a drying process can be dispensed with, an efficient film molding operation becomes possible.

[0101]

There are no special restrictions on the melt extrusion temperature on an occasion where the polylactic acid or lactic acid-type polyester is molded into a film, although

the temperature is normally designated within a range of 150 ~ 250°C. The melt-extruded sheet is cast for achieving a specified thickness and, if necessary, cooled. On this occasion, a homogeneous film or sheet is prepared by discriminately using a touch roll or air knife in a case where the film thickness is large and an electrostatic pinning in a case where the same is small. The lip gap at the time of melt extrusion is designated within a range of 0.2 ~ 3.0 mm, although a range of 0.2 ~ 1.5 mm is desirable in consideration of film moldability.

[0102]

Next, laminating methods will be concretely explained. In a case where a heat seal film is prepared based on the co-extrusion film molding method, a substrate layer & a heat seal layer are melted & kneaded within separate extruders, laminated within a T die or within a feed block at an anterior stage, and then transmitted through the T die for forming a film. The extrusion film molding procedures & conditions are fundamentally similar to the above-mentioned ones.

[0103]

In a case where the adhesive strength between the substrate layer & heat seal layer is inferior, it is also possible to configure an adhesive layer as an intermediate layer. Resins used favorably for said adhesive layer are instantiated by copolymers obtained by introducing special functional groups to polyolefins, etc., butene copolymers,

polyethyleneimine, modified celluloses, etc. It is desirable for the thickness of the adhesive layer to be confined to a range of 0.5 ~ 20 μm .

[0104]

According to the melt extrusion lamination method, a substrate layer transmitted by a feeder and a heat seal layer guided to the T die of a laminator from an extruder are mutually adhered & laminated within the laminator. Extrusion film molding procedures & conditions for the heat seal layer are fundamentally similar to the above-mentioned ones. In a case where the adhesive strength between the substrate layer & heat seal layer is inferior, it is also possible to improve the adhesion friendliness of the substrate layer by subjecting, prior to the delivery of the same to the laminator, the same to a corona discharge treatment, a flame plasma treatment, a chemical etching treatment (e.g., chromic acid treatment, etc.), ozone and/or ultraviolet surface treatment, sandblast treatment for forming surface depressions & protrusions, etc., or the adhesion friendliness of the same may instead be improved by selecting an appropriate anchor coating agent.

[0105]

Lamination methods for mutually pasting preliminarily prepared substrate & heat seal layers are instantiated by wet lamination, dry lamination, etc. In these cases, an

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adhesive must be coated on the substrate layer or heat seal layer prior to lamination. Adhesives used for wet lamination are instantiated by proteinous types such as casein, gelatin, etc., water-containing carbonaceous types such as starches, cellulose derivatives, etc., and synthetic resin types such as vinyl acetate, acrylic acid esters, acrylic-modified vinyl acetate, ethylene-vinyl acetate copolymer, etc.

[0106]

Adhesives used for dry lamination are instantiated by single-liquid reactive types obtained by integrating isocyanato groups with terminals of polyether polyurethane polyisocyanate, polyester polyurethane polyisocyanate, etc. and double-liquid reactive urethane types used by mixing main agents in possession of hydroxyl groups ascribed to polyester resins (e.g., polyester polyol, polyester polyurethane polyol, etc.) or polyether resins (e.g., polyether polyurethane polyol, etc.) with curing agents in possession of isocyanato groups. It is desirable for the coating rates of these adhesives to be designated within a range of approximately 1 ~ 5 g/m².

[0107]

The "heat resistance" as it is referred to in the present invention signifies a practical heat resistance level at which a film or sheet or processed object thereof retains some elasticity at the processing temperature or at the time or use without adversely affecting the physical appearance thereof or entailing deformation. The film or sheet or

processed objects thereof (e.g., bags, cases, light-weight containers, etc.) become exposed to hermetic states within transportation containers, warehouses, etc. during normal transportation & storage periods, and accordingly, it is not uncommon for them to become exposed to atmospheric temperatures of 50°C or above in the summer unless temperature management measures are orchestrated. Heat-resistant temperatures higher than this threshold are therefore necessary from a practical point of view.

[0108]

The lactic acid-type polyester composition (A) used for the substrate layer is crystallized for the purpose of conferring heat resistance onto the same, and as a method for thermally treating the same, the heat set method will be explained. The substrate layer that uses the lactic acid-type polyester composition (A) alone may be subjected to the heat set operation, or a laminate of the substrate layer & heat seal layer may instead be treated.

[0109]

There are no special restrictions on the temperature & time, although it is desirable, from the standpoint of achieving the optimal crystallization rate, for the heating temperature to be confined to a range from a level 40°C lower than the crystallization temperature (T_c) of the lactic acid-type polyester composition (A) to a level lower than the melting point (T_m) of the same. Above all, it is especially desirable, from the standpoint of achieving a favorable

surface state & favorable heat resistance, for the heat set temperature to be designated within a range from the crystallization temperature (T_c) to a level 40°C higher than the former.

[0110]

In a case where a stretching treatment is performed before or during the heat set treatment, furthermore, the crystallization rate can be accelerated, and the heat resistance can be improved based on a brief thermal treatment with a duration of approximately 5 ~ 30 sec. Since this treatment is accompanied by crystallization ascribed to orientation, furthermore, the heat resistance can be improved in a state where a favorable transparency characteristic of the lactic acid-type polyester composition is being preserved.

[0111]

There are no special restrictions on such stretching methods, although a sheet prevailing immediately after the melt extrusion of the lactic acid-type polyester or after the preservation thereof may be subjected to any treatment selected from among rolling, lengthwise monoaxial stretching, widthwise monoaxial stretching, simultaneous biaxial stretching, & consecutive biaxial stretching. Moreover, the substrate layer that uses the lactic acid-type polyester composition (A) alone may be subjected to such a stretching treatment, or a laminate of the substrate layer & heat seal layer may instead be stretched.

[0112]

It is desirable for the heating temperature on this occasion to be designated within a range from the glass transition point (T_g) of the substrate layer to level lower than the melting point of the same, whereas a temperature range from said glass transition point (T_g) to a level 50°C higher than said glass transition point is especially desirable, and above all, a temperature range $10 \sim 40^{\circ}\text{C}$ higher than the glass transition point (T_g) of the substrate layer is particularly desirable from the standpoint of optimizing the sheet surface state. It is desirable, from the standpoint of optimizing the surface state & transparency, for the area stretching draw ratio to be confined to a range of $1.4 \sim 16$ equivalents, preferably $2 \sim 16$ equivalents.

[0113]

Heat set methods are instantiated by a method wherein a target is heated over a specified time by using a forcibly created air contercurrent or radiation heat (e.g., infrared heater, etc.) and a method wherein a target is contacted with & heated by a hot panel, mold, or roll over a specified time. A method that uses a device called "tenter," in particular, is capable of continuously heat setting a film or sheet by forcibly generating a countercurrent of heated air, and accordingly, an excellent productivity can be achieved. Since this device targets stretching treatments, it is accordingly capable of completing stretching & heat set

operations within a brief period and of ensuring an excellent productivity. It is capable of efficiently crystallizing a heat seal film.

[0114]

In a case where a heat seal film is molded, by means of such thermal molding methods as vacuum molding, vacuum compressed air molding, hot panel compressed air molding, deep draw vacuum molding, etc., into light-weight containers for packaging, in rigid manners, such contents as foods, beverages, chemicals, non-durable consumer goods, etc., it is desirable for the heat set operation to be executed on a molding mold. There are no special restrictions on the heat set conditions on this occasion, namely the mold temperature & time, although the temperature may be inferred from the previously mentioned heat set temperature.

[0115]

The heat seal film of the present invention bears a heat resistance entailing no practical problems in general household settings, namely at least 60°C, and bears, at or below a temperature 20°C lower than the melting point of the lactic acid-type polyester composition (A), a minimal value of the storage modulus (E') of at least 40 MPa as it is stipulated by a test method on the temperature dependence of dynamic viscoelasticity (JIS-K-7198, method A).

[0116]

In a case where the storage modulus (E') is lower than 40 MPa, it becomes impossible to achieve a favorable

elasticity at 50 ~ 60°C, as a result of which a container becomes incapable of supporting filled contents as a result of deformation due to the load of said contents. It is desirable, in a case where the flexibility at the time of normal temperature use is also taken into consideration, for the storage modulus (E') to be confined to a range bearing a maximum of 4,000 MPa. In a case where a high heat-resistant temperature of 80°C or above is sought, furthermore, it is more desirable for the storage modulus (E') to be designated at 90 MPa or above.

[0117]

This test on the temperature dependence of dynamic viscoelasticity is conducted at a temperature elevation rate of 2°C/min. The glass transition point (T_g), crystallization temperature (T_c), & melting point (T_m) as they are referred to in the present invention correspond respectively to T_{ig} , T_{pc} , & T_{pm} as they are stipulated by JIS-K-7121, and the temperature elevation rate is set at 10°C/min. The "non-crystalline lactic acid-type polyester" as it is hereby referred to signifies a polymer on which no melting point peak is acknowledged according to JIS-K-7121. The softening point is measured in compliance with JIS-K-7206, method A.

[0118]

The heat seal film of the present invention, furthermore, exhibits an excellent impact resistance attributed to the lactic acid-type polyester composition used for the substrate layer or heat seal layer. A laminate film

constituted by a 250 μm substrate layer & a 15 μm heat seal layer, for example, bears an excellent DuPont impact strength of at least 0.2 J,

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preferably 0.3 ~ 5 J, in a stretched or yet-to-be-stretched state, and, in a case where it has been stretched & heat set, an excellent film impact profile of at least 1 J, preferably 1 ~ 10 J.

[0119]

The heat seal film of the present invention, furthermore, exhibits an excellent flexibility attributed to the lactic acid-type polyester composition used for the substrate layer or heat seal layer. A laminate film constituted by a 250 μm substrate layer & a 15 μm heat seal layer, for example, bears an excellent storage modulus (E') corresponding to a range of 0.5 ~ 3.0 GPa, preferably 0.6 ~ 2.4 GPa, according to a measurement method in compliance with JIS-K-7198, method A.

[0120]

The heat seal film of the present invention exhibits an excellent bleedout inhibitory effect attributed either to the lactic acid-type polyester composition used for the substrate layer or to the polylactic acid or lactic acid-type polyester composition used for the heat seal layer, and in particular, the same is desirable since it exhibits an excellent bleedout inhibitory effect even as a stretched film or sheet. In a case where a 10 \times 10 cm square yet-to-be-stretched sheet with

a thickness of 250 μm or a stretched sheet with a thickness of 35 μm is left unattended within a thermostat & humidistat vessel at 35°C & at a humidity of 80%, for example, no bleedout occurs on the surface of said molded product for at least 60 days.

[0121]

In a case where the heat seal layer of the heat seal film of the present invention is configured as mutually opposing sealing planes, an excellent sealing strength can be achieved. Even in a case where the substrate layer & heat seal layer are designated as sealing planes, too, an effective sealing strength can be achieved. The lower limit of the sealing strength after thermal melt adhesion in terms of the measurement value in compliance with JIS-Z-1710, for example, is at least 1 N/15 mm, more preferably at least 2 N/15 mm, even more preferably at least 4 N/15 mm, or most preferably at least 8 N/15 mm. There are no special restrictions on the upper limit of the same, although it may be designated at 50 N/mm or below, preferably 15 N/mm or below. In the so-called "easy-open-seal" field requiring a relatively tenuous sealing strength, for example, the strength requirement is approximately 4 ~ 8 N/15 mm, whereas a strength of at least 8 N/15 mm is necessary in fields requiring relatively high sealing strengths, whereas the heat seal film of the present invention can be used in diverse fields involving such performance requirements.

[0122]

The temperature at which the thermal melt adhesion of the heat seal film of the present invention becomes possible (sealing initialization temperature) coincides with the vicinity of 80°C. A favorable sealing strength can be achieved by executing thermal melt adhesion at or above this temperature.

[0123]

A heat seal film comprising of a thermally melt-adherable lactic acid-type polymer laminate of the present invention, furthermore, can be used as a packaging container required to meet a general heat resistance, and it is especially desirable for manufacturing packaging containers such as packaging bag or cases used for packaging or storage purposes as well as, by means of thermal molding, lightweight containers.

[0124]

The "packaging bag" as it is hereby referred to encompasses generally used bags abiding in flat plane or, in some cases, steric packaging morphological states provided by folding or, by such means as adhesion, etc., sealing synthetic resin films. Packaging targets for such containers are instantiated by foods (e.g., vegetables, confectionaries, bread, etc.), non-durable consumer goods, rice, fertilizers, etc., whereas the hereby obtained heat seal film can be used for these diverse applications as folded or thermally melt-adhered packaging bags.

[0125]

The "case" signifies a steric packaging material prepared by folding a sheet into a box, etc. or processing the same into a steric cylindrical shape without recourse to folding and, if necessary, by adhering & joining terminal units thereof by means of thermal melt adhesion, etc. without recourse to thermal molding means such as vacuum molding, compressed air molding, etc. Packaging targets calling for their uses are instantiated by cosmetic products, school/office supplies, compact electric appliances, toys, non-durable consumer goods, etc.

[0126]

Another embodiment of so-called "case," furthermore, pertains to a structure for housing documents, etc. on a flat plane provided by folding either edge plane & by thermally melt-adhering the other or by thermally melt-adhering two sides without closing the remaining two sides. The hereby obtained heat seal film can be used for these diverse applications as folded and/or thermally melt-adhered cases.

[0127]

The "light-weight container" signifies a packaging material obtained by sterically molding a film or sheet by means of thermal molding methods such as vacuum molding, vacuum compressed air molding, hot panel compressed air molding, deep draw vacuum molding, etc. Such materials are classified, depending on the morphologies thereof, into mainframes & lids or trays, food packs, blister packs, PTP packaging materials, cups for filling liquids, etc.

Packaging targets for light-weight containers include solid foods (e.g., vegetables, animal meats, gourmet dishes, confectionaries, bread, fried foods, etc.), fillable foods (e.g., jellies, jams, puddings, etc.), beverages (e.g., milk products, juices, etc.), chemicals (e.g., tablets, etc.), non-durable consumer goods, etc.

[0128]

The heat seal film obtained in the present invention bears an excellent thermal melt adhesion potential & routinely expected heat resistance and can therefore be used appropriately as packaging materials designed to package or store various foods, beverages, chemicals, non-durable consumer goods, etc., especially as bags, cases, & thermally molded light-weight containers.

[0129]

(Application examples)

The present invention will be explained with reference to application examples, although the present invention is not limited to them. In these application examples, "parts" & "%" respectively signify "parts by weight" & "wt%" unless otherwise qualified.

[0130]

The respective measurements & evaluations of the present application examples were rendered based on the following methods.

(1): Sealing strength

The sealing strength was measured as follows. The respective heat seal layers of a pair of obtained laminate films were mutually contacted as sealing planes and then thermally melt-adhered by using a heat sealer (manufactured by Tester Sangyo Co.). Subsequently, a 180° peeling test was conducted by using a tensile tester (manufactured by Shimazu Mfg. Co.), and the thermal melt adhesion adhesive strength based on the heat seal method was designated as the sealing strength.

[0131]

The sealing conditions were designated as follows: Seal bar temperature: 60 ~ 140°C; sealing pressure: 2 kgf/cm² (1.9 × 10⁵ Pa); sealing time: 1 sec. (dimensions of seal bar used: 10 × 300 mm). The sealing strength was measured based on a method in

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compliance with JIS-Z-1707.

[0132]

(2): Heat resistance

The heat resistance was evaluated as follows. In other words, an obtained laminate film was cut into a square with a side length of 20 cm, and after a weight of 300 g had been placed at the center of the same, the four corners of the same were bound together in such a way to wrap said weight for preparing a simple test bag. The obtained bag was

suspended within an air oven bearing a test temperature of 60°C or 80°C in a state where the bound portion thereof faced upward, and the film state attributed to the effect of the weight after a 20-min. period was observed. The length of the suspended test bag was adjusted at 13.5 cm. In a case where no particular variation was acknowledged, "O" was rendered (test bag length of less than 14 cm), whereas in a case where the bag was significantly stretched & deformed by the weight (test bag length of over 15 cm) or where the weight dropped due to a bag fracture, "x" was rendered, whereas their intermediate state was evaluated as "Δ."

[0133]

(3): Storage modulus

The storage modulus (E') was measured in terms either of the storage modulus (E') at a temperature 20°C lower than the melting point of the crystalline lactic acid-type polymer (A) or of the storage modulus (E') at 20°C in compliance with JIS-K-7198, method A.

(4): Transparency

The transparency was evaluated by calculating the haze value based on a method in compliance with JIS-K-7105.

(5): Thermal properties

The melting point, glass transition point, & crystallization temperature of each resin were calculated

based on a method in compliance with JIS-K-7121. The resin softening point was calculated based on a method in compliance with JIS-K-7206.

(6): Biodegradability

The biodegradability was evaluated as follows. In other words, 5 kg of raw rubbish was poured into an outdoor compost (volume: 100 L), and a square testpiece with a side length of 10 cm cut out of an obtained laminate film was placed atop the resulting pile. A raw rubbish layer with a thickness of approximately 5 cm was placed atop said testpiece, and the state of the testpiece was evaluated by the naked eye 1 month later. Incidentally, this test was conducted in the summer. The evaluation criteria were as follows: In a case where the retention of the shape was difficult due to significant degradations of physical properties, "O" was rendered, whereas in a case where the shape was retained despite deformation and/or blanching, "Δ" was rendered, whereas in a case where the state prior to the beginning of the test was retained without entailing blanching, deformation, etc., "×" was rendered.

[0134]

(7): Impact strength evaluation

A bell bearing a specified weight was dropped from a variable height incremented by an equal interval, and the 50% destruction energy of the obtained sheet was calculated based

on the presence or absence of destruction based on the DuPont impact strength measurement method stipulated by JIS-K-5400. The portion of the weight impacting the sheet was made of a steel, and a smooth hemispherical weight with a radius of 6.3 mm was used (a DuPont impact tester manufactured by Ueshima Mfg. Co was used).

(8): Bleedout tendency

The bleedout tendency was measured as follows. A film or sheet was left unattended within a thermostat & humidistat vessel RP-2F (manufactured by Tabai Espec Corp.) wherein the temperature & humidity were maintained respectively at 35°C & 80%. The film state was observed daily, and evaluations were rendered in terms of the number of days elapsed prior to the beginning of bleedout.

[0135]

<Manufacturing Examples>

Manufacturing Example 1: Preparation of polyester unit (b-1)

After 100 parts by weight of sebacic acid and propylene glycol (1.35 molar equivalents with respect to a molar equivalent of dicarboxylic acid) had been charged into a 1 L flask equipped with an agitation mechanism, a rectifier, & a gas introduction tube, the contents were heated & agitated under the pervasion of a nitrogen gas stream in a state where

the temperature was being elevated from 150°C at a rate of 10°C per hour.

[0136]

The temperature was elevated eventually to 220°C in a state where concomitantly generated water was being distilled & removed, and after 80 ppm of a titanium tetrabutoxide monomer had been added as a transesterification catalyst 1 hour later, the pressure was lowered to 0.1 KPa, and the contents were agitated over a 6-hour period. As a result, an aliphatic polyester (b-1) was obtained as a polyester unit. Measurements were rendered by means of gel permeation chromatography (abbreviated as "GPC," HLC-8020, manufactured by Toso Co.; column temperature: 40°C; tetrahydrofuran solvent used; same in subsequent references), as a result of which the numerical average molecular weight & weight-based average molecular weight of this polymer were respectively 28,000 & 52,000.

[0137]

Manufacturing Example 2: Preparation of polyester unit (b-2)

After 100 parts by weight of succinic acid (hereafter abbreviated as "SuA") and propylene glycol (1.35 molar equivalents with respect to a molar equivalent of dicarboxylic acid) had been charged into a 1 L flask equipped with an agitation mechanism, a rectifier, & a gas introduction tube, the contents were heated & agitated under the pervasion of a nitrogen gas stream in a state where the

temperature was being elevated from 150°C at a rate of 10°C per hour. The temperature was elevated eventually to 220°C in a state where concomitantly generated water was being distilled & removed, and after 70 ppm of hafnium tetrachloride had then been added, the contents were agitated. The pressure was lowered to 0.1 KPa 3 hours later, and after the contents had then been agitated over a 6-hour period, an aliphatic polyester (b-2) was obtained as a polyester unit bearing a numerical average molecular weight (Mn) of 20,000 & a weight-based average molecular weight (Mw) of 30,000 based on GPC polystyrene standards.

[0138]

Manufacturing Example 3: Preparations of lactic acid-type polyesters (A1-1) & (A1-2)

After 50 parts by weight of the aliphatic polyester (b-1) or (b-2) prepared earlier, 50 parts by weight of L-lactide, and 10 parts by weight of toluene with respect to the combined sum of said lactide & each polyester had been collected within a separable flask, the contents were melted/solubilized at 180°C. After a homogeneous solution had been obtained, 300 ppm of tin octanate was added, and the contents were agitated at 180°C over a 2.5-hour period.

[0139]

After the polymerization had been completed, 600 ppm of ethylhexanoic acid phosphate was added, and after the pressure had been lowered to 0.5 KPa, the contents were agitated over

a 1-hour period, and the residual lactide was removed. The lactic acid-type polyester (A1-1) obtained from the aliphatic polyester (b-1) bore, according to GPC, a numerical average molecular weight of 33,000 & a weight-based average molecular weight of 57,000 and a glass transition point (Tg) of 53°C, whereas the lactic acid-type polyester (A1-2) obtained from the aliphatic polyester (b-2) bore, according to GPC, a numerical average molecular weight of 24,000 & a weight-based average molecular weight of 36,000 and a glass transition point (Tg) of 57°C.

[0140]

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Manufacturing Example 4: Preparations of lactic acid-type polyesters (B1-1) & (B1-2)

After 50 parts by weight of the aliphatic polyester (b-1) or (b-2) prepared earlier, 45 parts by weight of L-lactide, 5 parts by weight of D-lactide, and 10 parts by weight of toluene with respect to the combined sum of these lactides & each polyester had been collected within a separable flask, the contents were melted/solubilized at 180°C. After a homogeneous solution had been obtained, 300 ppm of tin octanate was added, and the contents were agitated at 180°C over a 2.5-hour period. After the polymerization had been completed, 600 ppm of ethylhexanoic acid phosphate was added, and after the pressure had been lowered to 0.5 KPa, the contents were agitated over a 1-hour period, and the

residual lactide was removed. The lactic acid-type polyester (B1-1) obtained from the aliphatic polyester (b-1) bore, according to GPC, a numerical average molecular weight of 33,000 & a weight-based average molecular weight of 57,000, whereas the lactic acid-type polyester (B1-2) obtained from the aliphatic polyester (b-2) bore, according to GPC, a numerical average molecular weight of 24,000 & a weight-based average molecular weight of 36,000.

[0141]

Manufacturing Example 5: Preparation of polylactic acid (P1)

After [100 parts by weight of?] L-lactide had been agitated within an inert gas atmosphere at a temperature of 185°C over a 1-hour period, 0.02 part by weight of tin octanate was added as an esterification catalyst, and the contents were reacted over an 8-hour period. After 0.04 part by weight of an acidic phosphoric acid ester had subsequently been added as a deactivating agent, the contents were kneaded. The obtained polylactic acid (hereafter referred to as "P1") was a colorless & transparent resin bearing a weight-based average molecular weight of 250,000 (according to GPC measurement results), a glass transition point (T_g) of 59°C, a crystallization temperature (T_c) of 110°C, and a melting point (T_m) of 176°C.

[0142]

Manufacturing Example 6: Preparation of polylactic acid (P2)

After [100 parts by weight of?] a mixture of 70 mol% of L-lactide & 30 mol% of D-lactide had been agitated within an inert gas atmosphere at a temperature of 165°C over a 1-hour period, 0.02 part by weight of tin octanate was added as an esterification catalyst, and the contents were then reacted over an 8-hour period. After 0.04 part by weight of an acidic phosphoric acid ester had subsequently been added as a deactivating agent, the contents were kneaded. The obtained polylactic acid (hereafter referred to as "P2") was a colorless & transparent resin bearing a weight-based average molecular weight of 270,000 (according to GPC measurement results) & a glass transition point (Tg) of 52°C, whereas no melting point was acknowledged.

[0143]

<Reference Examples>

Reference Example 1

The lactic acid-type polyester composition (A) used as the substrate layer of the heat seal film of the present invention and a single-layer film or sheet comprising of said composition (A) were subjected to the following evaluation tests.

[0144]

{Evaluations of lactic acid-type polyester composition (A)}

The polylactic acid (abbreviated as "PLA") shown in Table I and the lactic acid-type polyester (A1-1) obtained in Manufacturing Example 1 were heated & dried at 100°C at a reduced pressure over a 6-hour period, as a result of which a lactic acid-type polyester composition (A) was obtained. Its glass transition point, melting point, storage modulus (E') at 20°C, and IZOD impact strength were measured, and the obtained results are summarized in Table I.

[0145]

(Evaluations of DuPont impact value & bleedout tendency of film)

The polylactic acid (abbreviated as "PLA") shown in Table I and the lactic acid-type polyester (A1-1) were heated & dried at 100°C at a reduced pressure over a 6-hour period, as a result of which a lactic acid-type polyester composition (A) was obtained. 3.3 g of this composition & a PET sheet with a thickness of 250 μm which had been punched into a 10 cm \times 10 cm square shape were sandwiched by PET sheets with a thickness of 100 μm each, and the obtained laminate structure was pressed under a pressure of 20 MPa over a 1-min. period in a state where it was heated & melted at 190°C. The obtained film was processed with a water-cooled press machine over a 10-min. period, and after the film comprising of said composition had been retrieved, it was left unattended at room temperature over a 24-min. period. The DuPont impact value & bleedout tendency of the obtained 10 cm \times 10 cm film

with a thickness of 250 μm were measured. The results are shown in Table I.

[0146]

(Preparation of biaxially stretched & heat set film)

The polylactic acid (abbreviated as "PLA") shown in Table I and the lactic acid-type polyester (A1-1) were heated & dried at 100°C at a reduced pressure over a 6-hour period, as a result of which a lactic acid-type polyester composition (A) was obtained. After this composition had been pressed by using a compact heat press at 195°C & 5 MPa over a 3-min. period, it was rapidly cooled, and after a 200 μm film (length: 12 cm; width: 12 cm) had been thus prepared, it was consecutively stretched by using a biaxially stretching device (manufactured by Iwamoto Mfg. Co.) at an identical draw ratio of 2.5 along both lengthwise & widthwise directions at a chuck interval of 10 cm, at a stretching temperature of 60°C, & at a stretching rate of 10 mm/sec. and then heat set within an air oven at 140°C over a 50-sec. period, as a result of which a biaxially stretched & heat set film with a thickness of approximately 35 μm was obtained. The DuPont impact value & bleedout tendency of the biaxially stretched & heat set film thus obtained were measured. The obtained results are summarized in Table I.

[0147]

Comparative Reference Example 1

Evaluations and measurement tests similar to their respective counterparts of Reference Example 1 were carried out by using the polylactic acid (P1).

[0148]

Comparative Reference Example 2

After 10 parts by weight of an aliphatic polyester (weight-based average molecular weight: 35,000; sebacic acid: 50 mol%; propylene glycol: 50 mol%) had been added to 100 parts by weight of L-lactide, the atmosphere was substituted with an inert gas, and after the contents had then been mixed at 170°C over a 1-hour period, 0.02 part by weight of tin octanate was added as an esterification catalyst, and the contents were then reacted over an 8-hour period. After 0.04 part by weight of an acidic phosphoric acid ester had subsequently been added as a deactivating agent, the contents were kneaded, as a result of which a polymer (A') was obtained. The obtained polymer (A') bore a weight-based average molecular weight of 110,000 (according to GPC measurement results), a glass transition point (T_g) of 49°C, a crystallization temperature (T_c) of 93°C, and a melting point (T_m) of 162°C. This polymer (A') was subjected to evaluations & measurement tests according to procedures respectively similar to their counterparts of Reference Example 1.

[0149]

Table I
(15)

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27		28		
		参考例 1	比較参考例 1	比較参考例 2
ポリ乳酸	ポリ乳酸名	P 1	P 1	—
	分子量(Mw)(万)	25	25	—
	分子量(Mn)(万)	16	16	—
	仕込量 (重量部)	100	100	0
乳酸系ポリエステル	分子量(Mw)(万)	5.7	—	11
	分子量(Mn)(万)	3.3	—	6.4
	仕込量 (重量部)	10	0	100
組成物、 又はポリマー	T _g (°C)	53	60	55
	mp (°C)	172	175	168
	貯蔵弾性率(GPa)20°C	2.2	3.5	2.1
	IZOD 衝撃強度(KJ/m ²)	15.1	2.0	2.2
250 μm	デュポン衝撃値 (J)	0.48	0.10	0.15
フィルム	ブリード開始日数	1年以上	1年以上	6ヶ月
35 μm 2軸延伸フィルム	746N/バケ(J)	3	0.7	2
伸熱引破力	貯蔵弾性率(GPa)20°C	2.7	3.5	2.1
	ブリード開始日数	1年以上	—	2日

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[(1): Reference Example; (2): Comparative Reference Example;
(3): Polylactic acid; (4): Lactic acid-type polyester; (5):
Composition or polymer; (6): 250 μm film; (7): 35 μm

biaxially stretched & heat set film; (8): Polylactic acid name; (9): Molecular weight (Mw) ($\times 10,000$); (10): Molecular weight (Mn) ($\times 10,000$); (11): Feeding rate (parts by weight); (12): Storage modulus (GPa), 20°C; (13): IZOD impact strength (KJ/cm²); (14): DuPont impact value (J); (15): Number of days prior to beginning of bleedout; (16): Film impact (J); (17): At least 1 year; (18): 6 months; (19): 2 days]

[0150]

<Application Examples: Preparations of heat seal films)

Application Examples 1 & 2

A lactic acid-type polyester composition (A) inclusive of the polylactic acid (hereafter abbreviated as "PLA") and lactic acid-type polyester (A1) shown in Table II to be used for a substrate layer and a polylactic acid or lactic acid-type polyester composition (B) inclusive of polylactic acid & a lactic acid-type polyester (B1) shown in Table II to be used for a heat seal layer were each blended, by using a drum tumbler, at the ratio shown in Table II and then vacuum-dried by using a vacuum dryer at 80°C over a 2-hour period. Subsequently, a laminate film with a thickness of 35 μm constituted by a substrate layer (20 μm) & a heat seal layer (15 μm) was extrusion-molded from a blend dried resin comprising of the lactic acid-type polyester composition (A)

designated for the substrate layer and the polylactic acid (hereafter abbreviated as "PLA") or lactic acid-type polyester composition (B) inclusive of polylactic acid & the lactic acid-type polyester (B1) designated for the heat seal layer by using a co-extruding machine (manufactured by Tanabe Plastic Co.).

[0151]

The obtained film was heat set within a 100°C air oven over a 10-min. period. The following aspects of the obtained laminate film were evaluated. Measurement results respectively on the thermal physical property value, sealing strength, heat resistance, storage modulus (E') at a temperature at least 20°C lower than the melting point, transparency, biodegradability, & bleedout tendency of the obtained laminate film are shown in Table II.

[0152]

The sealing initialization temperature of each laminate film coincided with the vicinity of 80°C, and a favorable sealing strength of at least 10 N/15 mm was exhibited at 90°C or above. Favorable heat resistances were acknowledged in an actual test using a weight at test temperatures of 60°C & 80°C. The minimal value of the storage modulus (E') of each laminate film at this time was at least 90 MPa. Moreover, the transparency & biodegradability of the prepared heat seal film were favorable.

[0153]

Application Example 3

A lactic acid-type polyester composition (A) inclusive of the polylactic acid (hereafter abbreviated as "PLA") and lactic acid-type polyester (A1) shown in Table II and a lactic acid-type polyester composition (B) inclusive of polylactic acid & a lactic acid-type polyester (B1) were each blended, by using a drum tumbler, at the ratio shown in Table II and then vacuum-dried by using a vacuum dryer at 80°C over a 2-hour period. Subsequently, a laminate film with a thickness of 140 μm constituted by a substrate layer (80 μm) & a heat seal layer (60 μm) was extrusion-molded by using a co-extruding machine (manufactured by Tanabe Plastic Co.) in such a way that the lactic acid-type polyester composition (A) & non-crystalline lactic acid-type polyester composition (B) will respectively constitute a substrate layer & a heat seal layer.

[0154]

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Next, a 35 μm stretched film was prepared [from said laminate film?] by using a single-shot biaxially stretching machine (manufactured by Iwamoto Mfg. Co.) at a stretching temperature of 70°C, over a pre-heating period of 5 min., at a stretching rate of 100%/min., at stretching draw ratios of 2×2 (length \times width) (area draw ratio: 4). The obtained film was subsequently pinched by & fixed to a frame and then heat set within a 100°C oven over a 20-sec. period.

[0155]

Measurement results respectively on the thermal physical property value, sealing strength, heat resistance, storage modulus (E') at a temperature 20°C lower than the melting point, transparency, biodegradability, & bleedout tendency of the obtained laminate film are shown in Table II. The sealing initialization temperature of the laminate film thus prepared coincided with the vicinity of 80°C, and a favorable sealing strength of 10 N/15 mm was exhibited at 90°C or above. No problems about heat resistances were acknowledged in an actual test using a weight at test temperatures of 60°C & 80°C. The transparency & biodegradability of the prepared heat seal film were favorable.

[0156]

Application Example 4

A lactic acid-type polyester composition (A) inclusive of the polylactic acid (hereafter abbreviated as "PLA") and lactic acid-type polyester (A1) shown in Table III and a lactic acid-type polyester composition (B) inclusive of polylactic acid & a lactic acid-type polyester (B1) were each blended, by using a drum tumbler, at the ratio shown in Table III and then vacuum-dried by using a vacuum dryer at 80°C over a 2-hour period. Subsequently, two types of laminate films with a thickness of 25 μ m each was extrusion-molded by using a co-extruding machine (manufactured by Tanabe Plastic Co.) in such a way that the lactic acid-type polyester composition (A) & non-crystalline lactic acid-type polyester

composition (B) will respectively constitute a substrate layer & a heat seal layer.

[0157]

At this juncture, a single-layer film constituted by the lactic acid-type polyester composition (A) alone was heat set within a 100°C air oven over a 10-min. period. Subsequently, a 30% gelatin solution was coated on either plane of each of these two types of films, pressed & adhered at 0.2 MPa, and then dried. As a result, a laminate film with a favorable physical appearance was obtained. Measurement results respectively on the thermal physical property value, sealing strength, heat resistance, storage modulus (E') at a temperature 20°C lower than the melting point, transparency, biodegradability, & bleedout tendency of the obtained laminate film are shown in Table III.

[0158]

The sealing initialization temperature of the laminate film thus prepared coincided with the vicinity of 80°C, and a favorable sealing strength of 10 N/15 mm was exhibited at 90°C or above. No problems about heat resistances were acknowledged in an actual test using a weight at test temperatures of 60°C & 80°C. The minimal value of the storage modulus (E') of each laminate film at this time was at least 90 MPa. The transparency & biodegradability of the prepared heat seal film were favorable.

[0159]

Application Example 4

A lactic acid-type polyester composition (A) inclusive of the polylactic acid (hereafter abbreviated as "PLA") and lactic acid-type polyester (A1) shown in Table III and a lactic acid-type polyester composition (B) inclusive of polylactic acid & a lactic acid-type polyester (B1) shown in Table III were each blended, by using a drum tumbler, at the ratio by using a drum tumbler and then vacuum-dried by using a vacuum dryer at 80°C over a 2-hour period. Subsequently, a laminate film with a thickness of 50 μm was extrusion-molded by using a co-extruding machine (manufactured by Tanabe Plastic Co.) by forming heat seal layers (15 μm) on both planes of a substrate layer (20 μm) in such a way that the lactic acid-type polyester composition (A) & non-crystalline lactic acid-type polyester composition (B) will respectively constitute said substrate layer & heat seal layers. The thermal physical property value, sealing strength, heat resistance, storage modulus (E') at a temperature 20°C lower than the melting point, transparency, biodegradability, & bleedout tendency of the obtained laminate film were then measured. The results are shown in Table III.

[0160]

The sealing initialization temperature of the laminate film thus prepared coincided with the vicinity of 80°C, and a favorable sealing strength was exhibited at 90°C or above. No problems about heat resistances were acknowledged in an actual test using a weight. The transparency &

biodegradability of the prepared heat seal film were favorable.

[0161]

Application Example 6

A lactic acid-type polyester composition (A) inclusive of the polylactic acid (hereafter abbreviated as "PLA") and lactic acid-type polyester (A1) shown in Table IV and a lactic acid-type polyester composition (B) inclusive of polylactic acid & a lactic acid-type polyester (B1) were each blended, by using a drum tumbler, at the ratio shown in Table IV and then vacuum-dried by using a vacuum dryer at 80°C over a 2-hour period. Subsequently, a laminate film with a thickness of 35 μm constituted by a substrate layer (20 μm) & a heat seal layer (15 μm) was extrusion-molded by using a co-extruding machine (manufactured by Tanabe Plastic Co.) in such a way that the lactic acid-type polyester composition (A) & non-crystalline lactic acid-type polyester composition (B) will respectively constitute a substrate layer & a heat seal layer.

[0162]

Subsequently, the obtained film was heat set within a 100°C air oven over a 10-min. period. At this juncture, one edge of the obtained laminate film was folded in a state where the heat seal layer constituted the inner plane of a packaging bag for forming the bottom portion of the packaging bag. Next, both sides of the folded portion were heat sealed

by using a heat sealer (manufactured by Tester Sangyo Co.), as a result of which a square (side length: 20 cm) packaging bag with one open side was prepared. The physical appearance of the packaging bag thus prepared was favorable, and the sealing strength of the two mutually sealed sides was also favorable. As sealing conditions, a seal bar temperature of 90°C, a sealing pressure of 0.2 MPa, & a sealing period of 1 sec. (dimensions of seal bar used: 10 × 300 mm) were designated.

[0163]

Measurement results respectively on the thermal physical property value, sealing strength, heat resistance, storage modulus (E') at a temperature 20°C lower than the melting point, transparency, biodegradability, & bleedout tendency of the obtained laminate film are shown in Table IV. No particular deformations or fractures were acknowledged on the packaging bag. The biodegradability was evaluated according to procedures similar to those in Application Examples 1 & 2 by using, as a testpiece, a packaging bag filled with raw rubbish, as a result of which a favorable biodegradability was acknowledged.

[0164]

Application Example 7

A lactic acid-type polyester composition (A) inclusive of the polylactic acid (hereafter abbreviated as "PLA") and lactic acid-type polyester (A1) shown in Table IV and a

lactic acid-type polyester composition (B) inclusive of polylactic acid & a lactic acid-type polyester (B1) were each blended, by using a drum tumbler, at the ratio shown in Table IV and then vacuum-dried by using a vacuum dryer at 80°C over a 2-hour period.

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Subsequently, a laminate film with a thickness of 35 μm constituted by a substrate layer (20 μm) & a heat seal layer (15 μm) was extrusion-molded by using a co-extruding machine (manufactured by Tanabe Plastic Co.) in such a way that the lactic acid-type polyester composition (A) & non-crystalline lactic acid-type polyester composition (B) will respectively constitute a substrate layer & a heat seal layer.

[0165]

Subsequently, the obtained film was heat set within a 100°C air oven over a 10-min. period. At this juncture, one edge of the obtained laminate film was folded in a state where the heat seal layer constituted the inner plane of a packaging bag for forming the bottom portion of the packaging bag. Next, both sides of the folded portion were rupture sealed, as a result of which a square (side length: 20 cm) packaging bag with one open side was prepared. The physical appearance of the packaging bag thus prepared was favorable, and the sealing strength of the two mutually sealed sides was also favorable. As a sealing condition, a seal bar temperature of 300°C was designated.

[0166]

The thermal physical property value, sealing strength, heat resistance, storage modulus (E') at a temperature 20°C lower than the melting point, transparency, biodegradability, & bleedout tendency of the obtained laminate film were respectively measured. The results are shown in Table IV. The heat resistance of the packaging bag was favorable, for it was accompanied by no particular deformations or fractures. The biodegradability was evaluated according to procedures similar to those in Application Examples 1 & 2 by using, as a testpiece, a packaging bag filled with raw rubbish, as a result of which a favorable biodegradability was acknowledged.

[0167]

Application Example 8

A lactic acid-type polyester composition (A) inclusive of the polylactic acid (hereafter abbreviated as "PLA") and lactic acid-type polyester (A1) shown in Table IV and a lactic acid-type polyester composition (B) inclusive of polylactic acid & a lactic acid-type polyester (B1) were each blended, by using a drum tumbler, at the ratio shown in Table IV and then vacuum-dried by using a vacuum dryer at 80°C over a 2-hour period. Subsequently, a laminate sheet with a thickness of 35 μm constituted by a substrate layer (20 μm) & a heat seal layer (15 μm) was extrusion-molded by using a co-extruding machine (manufactured by Tanabe Plastic Co.) in such a way that the lactic acid-type polyester composition

(A) & non-crystalline lactic acid-type polyester composition (B) will respectively constitute a substrate layer & a heat seal layer.

[0168]

Subsequently, the obtained sheet was heat set within a 100°C air oven over a 10-min. period. At this juncture, one edge of the obtained laminate film was folded in a state where the heat seal layer constituted the inner plane of a packaging bag for forming the bottom portion of the packaging bag. Next, both sides of the folded portion were impulse sealed, as a result of which a square (side length: 20 cm) packaging bag with one open side was prepared.

[0169]

The physical appearance of the packaging bag thus prepared was favorable, and the sealing strength of the two mutually sealed sides was also favorable. "Polysealer" (manufactured by Fuji Co.) was used as a sealing machine.

[0170]

Measurement results respectively on the thermal physical property value, sealing strength, heat resistance, storage modulus (E') at a temperature 20°C lower than the melting point, transparency, biodegradability, & bleedout tendency of the obtained laminate film are shown in Table IV. No particular deformations or fractures were acknowledged on the packaging bag in terms of the heat resistance thereof. The biodegradability was evaluated according to procedures similar to those in Application Examples 1 & 2 by using, as a

testpiece, a packaging bag filled with raw rubbish, as a result of which a favorable biodegradability was acknowledged.

[0171]

Application Example 9

A lactic acid-type polyester composition (A) inclusive of the polylactic acid (hereafter abbreviated as "PLA") and lactic acid-type polyester (A1) shown in Table IV and a lactic acid-type polyester composition (B) inclusive of polylactic acid & a lactic acid-type polyester (B1) were each blended, by using a drum tumbler, at the ratio shown in Table IV and then vacuum-dried by using a vacuum dryer at 80°C over a 2-hour period. Subsequently, a laminate sheet with a thickness of 115 μm constituted by a substrate layer (100 μm) & a heat seal layer (15 μm) was extrusion-molded by using a co-extruding machine (manufactured by Tanabe Plastic Co.) in such a way that the lactic acid-type polyester composition (A) & non-crystalline lactic acid-type polyester composition (B) will respectively constitute a substrate layer & a heat seal layer.

[0172]

Subsequently, the obtained sheet was heat set within a 100°C air oven over a 10-min. period. At this juncture, the obtained laminate sheet was curled in a cylindrical shape in a state where the heat seal layer constituted the inner plane of a case, and after both edges of the same had been

overlapped & heat sealed, the profile plane portion of a cylindrical case was prepared. The height & diameter of the cylinder were respectively 10 cm & 5 cm. The physical appearance of the sealed portion of the profile plane of the case thus prepared was favorable, and the sealing strength was also favorable. As sealing conditions, a seal bar temperature of 100°C, a sealing pressure of 0.2 MPa, & a sealing time of 1 sec. were designated.

[0173]

The thermal physical property value, sealing strength, heat resistance, storage modulus (E') at a temperature 20°C lower than the melting point, transparency, biodegradability, & bleedout tendency of the obtained laminate film were respectively measured. The results are shown in Table IV. A heat resistance test was conducted over a 20-min. period in a state where the prepared cylindrical case was being vertically erected within an air oven at a test temperature of 60°C or 80°C. No particular deformations or fractures were acknowledged. The biodegradability was evaluated according to procedures similar to those in Application Examples 1 & 2 by using, as a testpiece, a case filled with raw rubbish, as a result of which a favorable biodegradability was acknowledged.

[0174]

Application Example 10

A lactic acid-type polyester composition (A) inclusive of the polylactic acid (hereafter abbreviated as "PLA") and lactic acid-type polyester (A1) shown in Table IV and a lactic acid-type polyester composition (B) inclusive of polylactic acid & a lactic acid-type polyester (B1) were each blended, by using a drum tumbler, at the ratio shown in Table IV and then vacuum-dried by using a vacuum dryer at 80°C over a 2-hour period. Subsequently, a laminate sheet for vacuum molding with a thickness of 265 μm constituted by a substrate layer (250 μm) & a heat seal layer (15 μm) was extrusion-molded by using a co-extruding machine (manufactured by Tanabe Plastic Co.) in such a way that the lactic acid-type polyester composition (A) & non-crystalline lactic acid-type polyester composition (B) will respectively constitute a substrate layer & a heat seal layer.

[0175]

Moreover, a sealing laminate film with a thickness of 35 μm constituted by a 20 μm substrate layer & a 15 μm heat seal layer was likewise extrusion-molded. These films were each heat set within a 100°C air oven over a 10-min. period. Incidentally, the laminate sheet for vacuum molding was subjected to an impact strength evaluation. The impact value of said laminate sheet for vacuum molding was 0.35 J and favorable.

[0176]

Said sheet was molded, by means of vacuum molding, into an evaluation light-weight container by using a circular cup-

shaped mold with an open unit diameter of 55 mm & a draw ratio of 0.36 (female mold). The heat seal layer was configured at this time to

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constitute the inner side of the container, whereas the width of the flange unit of the molded product corresponding to the sealed portion was designated at 3 mm. As vacuum molding conditions, a heater temperature of 40°C, a heating period of 10 sec., a mold temperature of 80°C, and a molding period of 30 sec. were designated.

[0177]

Measurement results respectively on the thermal physical property value, sealing strength, heat resistance, storage modulus (E') at a temperature 20°C lower than the melting point, transparency, biodegradability, & bleedout tendency of the obtained laminate film are shown in Table IV. The heat resistance of the prepared cup was tested within an air oven over a 20-min. period at a test temperature of 60°C or 80°C. No particular shrinkage, deformation, etc. were acknowledged at 60°C, although some deformation was acknowledged at 80°C. Evaluations were rendered in terms of physical appearances (○: Favorable; ×: Shrinkage; Δ: Some deformation). Next, the cup & sealing film were heat sealed by using "Auto Cup Sealer" (manufactured by Sunrise System Co.) at a sealing temperature of 100°C & at a sealing pressure of 0.2 MPa over a 1-sec. sealing period. The respective heat seal layers were joined as sealed planes. The sealing strength of the

sealed light-weight container was favorable, and the sealed physical appearance of the same was also favorable.

[0178]

The biodegradability was evaluated according to procedures similar to those in Application Examples 1 & 2 by using, as a testpiece, a light-weight container filled with raw rubbish, as a result of which a favorable biodegradability was acknowledged.

[0179]

Table II

実施例			1	2	3
基材層	乳酸系ポリエステル(A1)		A1-1	A1-1	A1-2
	ポリ乳酸 100 部に対する乳酸系ポリエステル(A1)の添加量(部)		10	10	30
	ポリ乳酸		P1	P1	P1
	乳酸系ポリエステル組成物(A)の融点[℃]		175	175	174
	乳酸系ポリエステル組成物(A)の結晶化温度[℃]		110	115	110
ヒート	乳酸系ポリエステル(B1)		—	B1-1	B1-2
シール層	ポリ乳酸 100 部に対する乳酸系ポリエステル(B1)の添加量(部)		—	10	30
	ポリ乳酸		P2	P2	P2
	乳酸系ポリエステル組成物(B)の軟化温度 [℃]		52	51	51
	厚み[mm]		35	35	35
ヒート シール フィルム	ヘイズ値[%]		5	5	3
	耐熱性	60℃	○	○	○
		80℃	○	○	○
	E' [MPa]		150	130	100
	生分解性		○	○	○
	強度	80℃	4	3	2
		90℃	7	6	7
		100℃	8	8	8
		120℃	10	9	10
		140℃	10	9	10
		[N/15mm]			
	ブリード開始日数		1 年 以上	1 年 以上	1 年 以上

[(1): Application Example; (2): Substrate layer; (3): Heat seal layer; (4): Heat seal film; (5): Lactic acid-type polyester (A1); (6): Addition ratio of lactic acid-type polyester (A1) with respect to 100 parts of polylactic acid (parts); (7): Polylactic acid; (8): Melting point (°C) of lactic acid-type polyester composition (A); (9):

Crystallization temperature (°C) of lactic acid-type polyester composition (A); (10): Lactic acid-type polyester (B1); (11): Addition ratio of lactic acid-type polyester (B1) with respect to 100 parts of polylactic acid (parts); (12): Softening point (°C) of lactic acid-type polyester composition (B); (13): Thickness (μm); (14): Haze value (%); (15): Heat resistance; (16): Biodegradability; (17): Sealing strength (N/15 mm); (18): Number of days prior to beginning of bleedout; (19): At least 1 year]

[0180]

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Table III

実施例		4	5
基材層	乳酸系ポリエステル(A1)	A1-2	A1-1
	ポリ乳酸 100 部に対する乳酸系ポリエステル(A1)の添加量(部)	80	10
	ポリ乳酸	P1	P1
	乳酸系ポリエステル組成物(A)の融点[°C]	174	175
	乳酸系ポリエステル組成物(A)の結晶化温度[°C]	110	110
ヒート	乳酸系ポリエステル(B1)	B1-2	B1-1
シール層	ポリ乳酸 100 部に対する乳酸系ポリエステル(B1)の添加量(部)	80	10
	ポリ乳酸	P2	P2
	乳酸系ポリエステル組成物(B)の軟化温度 [°C]	51	51
ヒート シール フィルム	厚み[μm]	52	60
	ヘイズ値[%]	4	7
	耐熱性	60°C	○
		80°C	○
	E' [MPa]	100	130
	生分解性	○	○
	テーパー強度 [N/15mm]	80°C	2
		90°C	7
		100°C	8
		120°C	10
		140°C	10
	ブリード開始日数	1 年 以上	1 年 以上

[(1): Application Example; (2): Substrate layer; (3): Heat seal layer; (4): Heat seal film; (5): Lactic acid-type polyester (A1); (6): Addition ratio of lactic acid-type polyester (A1) with respect to 100 parts of polylactic acid

(parts); (7): Polylactic acid; (8): Melting point (°C) of lactic acid-type polyester composition (A); (9): Crystallization temperature (°C) of lactic acid-type polyester composition (A); (10): Lactic acid-type polyester (B1); (11): Addition ratio of lactic acid-type polyester (B1) with respect to 100 parts of polylactic acid (parts); (12): Softening point (°C) of lactic acid-type polyester composition (B); (13): Thickness (μm); (14): Haze value (%); (15): Heat resistance; (16): Biodegradability; (17): Sealing strength (N/15 mm); (18): Number of days prior to beginning of bleedout; (19): At least 1 year]

[0181]

Table IV

37		38				
実施例		6	7	8	9	10
基材層	乳酸系ポリエステル(A1)	A1-2	A1-2	A1-2	A1-1	A1-1
	ポリエステル 100 部に対する乳酸系ポリエステル(A1)の添加量(部)	30	30	50	10	10
	ポリ乳酸	P1	P1	P1	P1	P1
	乳酸系ポリエステル組成物(A)の融点[℃]	174	174	174	175	175
	乳酸系ポリエステル組成物(A)の結晶化温度[℃]	110	110	110	110	110
ヒート シール 層	乳酸系ポリエステル(B1)	B1-2	B1-2	B1-2	B1-1	B1-1
	ポリエステル 100 部に対する乳酸系ポリエステル(B1)の添加量(部)	30	10	30	10	10
	ポリ乳酸	P2	P2	P2	P2	P2
	乳酸系ポリエステル組成物(B)の軟化温度[℃]	52	52	52	51	51
ヒート シール フィルム	厚み[μm]	35	35	35	115	265
	ヘイズ値[%]	4	4	4	10	20
	耐熱性	60℃		○	○	○
		80℃		○	○	○
	E' [MPa]	100	100	100	130	120
Δ	生分解性	○	○	○	○	○
	ブリード開始日数	1 年 以上	1 年 以上	1 年 以上	1 年 以上	1 年 以上

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[(1): Application Example; (2): Substrate layer; (3): Heat seal layer; (4): Heat seal film; (5): Lactic acid-type polyester (A1); (6): Addition ratio of lactic acid-type polyester (A1) with respect to 100 parts of polylactic acid (parts); (7): Polylactic acid; (8): Melting point (°C) of lactic acid-type polyester composition (A); (9):

Crystallization temperature (°C) of lactic acid-type polyester composition (A); (10): Lactic acid-type polyester (B1); (11): Addition ratio of lactic acid-type polyester (B1) with respect to 100 parts of polylactic acid (parts); (12): Softening point ((C) of lactic acid-type polyester composition (B); (13): Thickness (μm); (14): Haze value (%); (15): Heat resistance; (16): Biodegradability; (17): Number of days prior to beginning of bleedout; (18): At least 1 year]

[0182]

Comparative Examples 1 & 2

A lactic acid-type polyester composition (A) inclusive of the polylactic acid (hereafter abbreviated as "PLA") and lactic acid-type polyester (A1) shown in Table V and a lactic acid-type polyester composition (B) inclusive of polylactic acid & a lactic acid-type polyester (B1) were each blended, by using a drum tumbler, at the ratio shown in Table V and then vacuum-dried by using a vacuum dryer at 80°C over a 2-hour period. As far as the present comparative example is concerned, a laminate film with a thickness of 35 μm constituted by a substrate layer (20 μm) & a heat seal layer (15 μm) was extrusion-molded by using a co-extruding machine (manufactured by Tanabe Plastic Co.) in such a way that the lactic acid-type polyester composition (A) & non-crystalline lactic acid-type polyester composition (B) will respectively constitute a heat seal layer & a substrate layer, and the

film thus molded was heat set within a 100°C air oven over a 10-min. period. As far as film strength measurements are concerned, the respective heat seal layers of a pair of the obtained laminate films were mutually joined, and after the sealing planes had been thermally melt-adhered by using a heat sealer (manufactured by Tester Sangyo Co.), the sealing strength was evaluated. Moreover, the thermal physical property value, sealing strength, heat resistance, storage modulus (E') at a temperature 20°C lower than the melting point, transparency, biodegradability, & bleedout tendency were respectively measured. The obtained results are shown in Table V. This film yielded no sealing strength.

[0183]

Comparative Example 3

A lactic acid-type polyester composition (A) inclusive of the polylactic acid (hereafter abbreviated as "PLA") and lactic acid-type polyester (A1) shown in Table V and a lactic acid-type polyester composition (B) inclusive of polylactic acid & a lactic acid-type polyester (B1) were each blended, by using a drum tumbler, at the ratio shown in Table V and then vacuum-dried by using a vacuum dryer at 80°C over a 2-hour period. As far as the present comparative example is concerned, a laminate film with a thickness of 140 μm constituted by a substrate layer (80 μm) & a heat seal layer (60 μm) was extrusion-molded in such a way that the lactic acid-type polyester composition (A) & non-crystalline lactic

acid-type polyester composition (B) will respectively constitute a heat seal layer & a

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substrate layer.

[0184]

Next, a 35 μm stretched film was prepared [from said laminate sheet?] by using a single-shot biaxially stretching machine (manufactured by Iwamoto Mfg. Co.) at a stretching temperature of 70°C, over a pre-heating period of 5 min., at a stretching rate of 100%/min., at stretching draw ratios of 2 \times 2 (length \times width) (area draw ratio: 4). The obtained film was subsequently pinched by & fixed to a square frame with a side length of 30 cm and then heat set within a 100°C oven over a 20-sec. period.

[0185]

As far as film strength measurements are concerned, the respective heat seal layers of a pair of the obtained laminate films were mutually joined, and after the sealing planes had been thermally melt-adhered by using a heat sealer (manufactured by Tester Sangyo Co.), the sealing strength was evaluated. Moreover, the thermal physical property value, sealing strength, heat resistance, storage modulus (E') at a temperature 20°C lower than the melting point, transparency, biodegradability, & bleedout tendency were respectively measured. The obtained results are shown in Table V. This film yielded no sealing strength.

[0186]

Table V

【表5】シール強度測定は、シール強度の測定は、【表5】

比較例		1	2	3
ヒートシール層	乳酸系ポリマー(A)	1	1	2
	ポリ乳酸 100 部に対する 乳酸系ポリマー(A)の添加量(部)	10	10	80
	ポリ乳酸	P1	P1	P1
	乳酸系ポリマー(A)の融点[°C]	176	176	174
	乳酸系ポリマー(A)の結晶化温度[°C]	110	110	110
基材層	乳酸系ポリマー(B)	—	1	2
	ポリ乳酸 100 部に対する 乳酸系ポリマー(B)の添加量(部)	—	10	80
	ポリ乳酸	P2	P2	P2
	乳酸系ポリマー(B)の軟化温度[°C]	52	51	51
ヒートシールフィルム	厚み[μm]	25	25	25
	ヘイズ値[%]	5	5	3
	耐熱性	60°C	○	○
		80°C	○	○
	ε' [MPa]	120	110	90
	生分解性	○	○	○
	シール強度	80°C	0	0
		90°C	0	0
		100°C	0	0
		120°C	0	0
		140°C	0	0
	ブリード開始日数	1年以 上	1年以 上	1年以 上

[(1): Comparative Example; (2): Heat seal layer; (3): Substrate layer; (4): Heat seal film; (5): Lactic acid-type

polyester (A1); (6): Addition ratio of lactic acid-type polyester (A1) with respect to 100 parts of polylactic acid (parts); (7): Polylactic acid; (8): Melting point (°C) of lactic acid-type polyester composition (A); (9): Crystallization temperature (°C) of lactic acid-type polyester composition (A); (10): Lactic acid-type polyester (B1); (11): Addition ratio of lactic acid-type polyester (B1) with respect to 100 parts of polylactic acid (parts); (12): Softening point (°C) of lactic acid-type polyester composition (B); (13): Thickness (μm); (14): Haze value (%); (15): Heat resistance; (16): Biodegradability; (17): Sealing strength (N/15 mm); (18): Number of days prior to beginning of bleedout; (19): At least 1 year]

[0187]

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Comparative Example 4

A lactic acid-type polyester composition (A) inclusive of the polylactic acid (hereafter abbreviated as "PLA") and lactic acid-type polyester (A1) shown in Table VI and a lactic acid-type polyester composition (B) inclusive of polylactic acid & a lactic acid-type polyester (B1) were each blended, by using a drum tumbler, at the ratio shown in Table VI and then vacuum-dried by using a vacuum dryer at 80°C over a 2-hour period. A laminate film with a thickness of 35 μm constituted by a substrate layer (20 μm) & a heat seal layer (15 μm) was extrusion-molded in such a way that the lactic

acid-type polyester composition (A) & non-crystalline lactic acid-type polyester composition (B) will respectively constitute a substrate layer & a heat seal layer.

[0188]

The heat resistance & transparency of the obtained laminate film were subsequently measured without heat setting the same. As far as the heat resistance of the laminate film thus prepared is concerned, fractures were acknowledged in an actual test using a weight at test temperatures of 60°C & 80°C. The minimal value of the storage modulus (E') of the laminate film at a temperature 20°C lower than the melting point of the same was 0 MPa, and thus, no heat resistance was acknowledged.

[0189]

Comparative Example 5

A lactic acid-type polyester composition (A) inclusive of the polylactic acid (hereafter abbreviated as "PLA") and lactic acid-type polyester (A1) shown in Table VI was blended, as a resin mixture by using a drum tumbler, at the ratio shown in Table VI and then vacuum-dried by using a vacuum dryer at 80°C over a 2-hour period. The lactic acid-type polyester composition (A) was subsequently extrusion-molded by using a co-extruding machine (manufactured by Tanabe Plastic Co.), and the obtained single-layer film with a thickness of 35 μm was heat set within a 100°C air oven over a 10-min. period.

[0190]

The sealing strength, heat resistance, & transparency of the obtained single-layer film were measured. The results are shown in Table VI. No heat sealing strength was acknowledged.

[0191]

Comparative Example 6

A lactic acid-type polyester composition (B) inclusive of the polylactic acid (hereafter abbreviated as "PLA") and lactic acid-type polyester (B1) shown in Table VI was blended, as a resin mixture by using a drum tumbler, at the ratio shown in Table VI and then vacuum-dried by using a vacuum dryer at 80°C over a 2-hour period. A single-layer film with a thickness of 35 μm was subsequently obtained by means of extrusion molding by using a co-extruding machine (manufactured by Tanabe Plastic Co.), and said film was heat set within a 100°C air oven over a 10-min. period. The sealing strength, heat resistance, transparency, biodegradability, & bleedout tendency of the obtained single-layer film were measured. The results are shown in Table VI. As far as the heat resistance of the laminate film [sic: Presumably "single-layer film"] thus prepared is concerned, fractures were acknowledged in an actual test using a weight at test temperatures of 60°C & 80°C. The minimal value of the storage modulus (E') of the laminate film [sic] was 0 MPa, and thus, no heat resistance was acknowledged.

[0192]

Comparative Example 7

After 10 parts by weight of an aliphatic polyester (weight-based average molecular weight: 35,000; sebacic acid: 50 mol%; propylene glycol: 50 mol%) had been added to 100 parts by weight of L-lactide, the atmosphere was substituted with an inert gas, and after the contents had then been mixed at 170°C over a 1-hour period, 0.02 part by weight of tin octanate was added as an esterification catalyst, and the contents were then reacted over an 8-hour period. After 0.04 part by weight of an acidic phosphoric acid ester had subsequently been added as a deactivating agent, the contents were kneaded, as a result of which a polymer (A') was obtained. The obtained polymer (A') bore a weight-based average molecular weight of 110,000 (according to GPC measurement results), a glass transition point (T_g) of 49°C, a crystallization temperature (T_c) of 93°C, and a melting point (T_m) of 162°C. This polymer (A') was scheduled to be used as a substrate layer.

[0193]

After 10 parts by weight of an aliphatic polyester (weight-based average molecular weight: 35,000; sebacic acid: 50 mol%; propylene glycol: 50 mol%) had been added to lactides (90 parts by weight of L-lactide & 10 parts by weight of D-lactide), the atmosphere was substituted with an inert gas, and after the contents had then been mixed at

170°C over a 1-hour period, 0.02 part by weight of tin octanate was added as an esterification catalyst, and the contents were then reacted over an 8-hour period. After 0.04 part by weight of an acidic phosphoric acid ester had subsequently been added as a deactivating agent, the contents were kneaded, as a result of which a polymer (B') was obtained. The obtained polymer (B') bore a weight-based average molecular weight of 110,000 (according to GPC measurement results), a glass transition point (T_g) of 48°C, & a crystallization temperature (T_c) of 48°C, although no melting point (T_m) was acknowledged. This polymer (B') was scheduled to be used as a heat seal layer. The respective polymers obtained above were vacuum-dried by using a vacuum dryer at 80°C over a 2-hour period. A laminate sheet with a thickness of 265 μm constituted by a substrate layer (250 μm) & a heat seal layer (15 μm) was subsequently extrusion-molded by using a co-extruding machine (manufactured by Tanabe Plastic Co.) in such a way that the polymer (A) & non-crystalline polymer (B') will respectively constitute a substrate layer & a heat seal layer.

[0194]

The impact strength of said laminate sheet was evaluated. The ascertained impact value was 0.15 J, which was judged to be inferior to that of the sheet prepared in Application Example 10 (0.35 J).

[0195]

Comparative Example 8

The polymer (A') & polymer (B') prepared in Comparative Example 7 were respectively vacuum-dried by using a vacuum dryer at 80°C over a 2-hour period. A laminate sheet with a thickness of 140 μm constituted by a substrate layer (80 μm) & a heat seal layer (60 μm) was subsequently extrusion-molded by using a co-extruding machine (manufactured by Tanabe Plastic Co.) in such a way that the polymer (A') & non-crystalline polymer (B') will respectively constitute a substrate layer & a heat seal layer. Next, a 35 μm stretched film was prepared [from said laminate sheet?] by using a single-shot biaxially stretching machine (manufactured by Iwamoto Mfg. Co.) at a stretching temperature of 70°C, over a pre-heating period of 5 min., at a stretching rate of 100%/min., at stretching draw ratios of 2×2 (length \times width) (area draw ratio: 4). The obtained film was subsequently pinched by & fixed to a frame and then heat set within a 100°C oven over a 20-sec. period. White deposits were observed on the surfaces (both planes) of the stretched laminate film 2 days after stretching.

[0196]

/23

Table VI

(23)

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比較例		4	5	6
乳酸系ポリ エステル組成 物(A)	乳酸系ポリエステル(A1)	1	1	—
	ポリ乳酸 100 部に対する乳酸系ポリエステル(A1)の添 加量(部)	10	10	—
	ポリ乳酸	P1	P1	—
	乳酸系ポリエステル(A)の融点[°C]	175	175	—
	乳酸系ポリエステル(A)の結晶化温度[°C]	110	110	—
酸系ポリ エステル組成 物(B)	乳酸系ポリエステル(B1)	1	—	1
	ポリ乳酸 100 部に対する 乳酸系ポリエステル(B1)の添加量(部)	10	—	10
	ポリ乳酸	P2	—	P2
	乳酸系ポリエステル(B)の軟化温度[°C]	51	—	52
積層フィ ルム、又は 単層フィ ルム	厚み[μm]	50	35	35
	ヘイズ値[%]	7	7	3
	耐熱性	60°C	○	○
		80°C	○	○
	E' [MPa]	0	0	0
	生分解性	○	○	○
	シールド度 [N/15mm]	80°C	2	0
		90°C	7	0
		100°C	8	0
		120°C	9	0
		140°C	9	0
	ブリード開始日数	1 年 以上	1 年 以上	1 年 以上

[(1): Comparative Example; (2): Lactic acid-type polyester composition (A); (3): Lactic acid-type polyester composition (B); (4): Laminate film or single-layer film; (5): Lactic acid-type polyester (A1); (6): Addition ratio of lactic acid-type polyester (A1) with respect to 100 parts of polylactic acid (parts); (7): Polylactic acid; (8): Melting point (°C) of lactic acid-type polyester composition (A); (9): Crystallization temperature (°C) of lactic acid-type polyester composition (A); (10): Lactic acid-type polyester (B1); (11): Addition ratio of lactic acid-type polyester (B1) with respect to 100 parts of polylactic acid (parts); (12): Softening point ((C) of lactic acid-type polyester composition (B); (13): Thickness (μm); (14): Haze value (%); (15): Heat resistance; (16): Biodegradability; (17): Sealing strength (N/15 mm); (18): Number of days prior to beginning of bleedout; (19): At least 1 year]

[0197]

(Effects of the invention)

The present invention is capable of providing a heat seal film bearing an excellent impact resistance, flexibility, heat resistance, & sealing strength as well as a low bleedout tendency, and in particular, a heat seal film comprising of a yet-to-be-stretched film or sheet bearing an excellent impact strength, flexibility, heat resistance, & sealing strength and/or a heat seal film comprising of a

stretched film or sheet bearing an excellent heat resistance & sealing strength as well as a low bleedout tendency.